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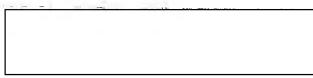
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REPORT T.A. 270
OF THE
GENERAL TECHNICAL DEPARTMENT T.N.O.
OF THE CENTRAL NATIONAL COUNCIL FOR APPLIED SCIENTIFIC
RESEARCH IN THE NETHERLANDS

Survey of water desalting investigations, in
particular the electrodialytic method.



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GENERAL TECHNICAL DEPARTMENT T.N.O.

The Hague

Report T.A. No 270

TITLE : Survey of water desalting investigations, in particular the electrodialytic method.

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- 3 -

OBJECT.

To find an economically justifiable method of desalting water for domestic, industrial and agricultural purposes.

METHOD.

Literature research was carried out into methods of desalting sea water and brackish water in general and into electrodialytic removal of salts from brackish and similar waters in particular.

An investigation was made into the factors determining energy consumption for electrodialysis.

Experimental investigations were made into the results obtainable by electrodialytic and electrolytic purification of water from about 1650 to about 500 mg sodium chloride per litre.

CONCLUSIONS.

1. It appears to be possible to desalt 1 m³ water from 1650 to 500 mg sodium chloride per litre at a cost of Fl. 0.37 per m³, while further reduction of this figure may be attained.
2. There are sound economic reasons for intensive continuation of research into electrodialytic desalting of brackish and similar waters.
3. As regards the most economic method for the desalting of seawater no proper comparison is yet possible between vapour compression distillation and electrolytic or electrodialytic purification methods.

C O N T E N T S

	pg.
I. <u>STARTING POINT TO THE INVESTIGATIONS.</u>	15
II. <u>GENERAL METHODS OF DESALTING WATER.</u>	18
A. Desalting methods for sea water.	18
B. The desalting of brackish waters.	24
III. <u>ELECTRODIALYTIC REMOVAL OF SALTS FROM BRACKISH AND SIMILAR WATERS.</u>	27
A. Introduction.	27
B. The principal patents relating to electro-dialytic desalting of water.	29
C. Brief survey of the literature on the electro-dialytic water desalting.	30
D. Review of the theoretical computations by Aten in the electrodialytic desalting of water in a three-compartment cell.	35
E. The experiments of Hoffmann.	42
F. The electrode processes.	43
IV. <u>ENERGY CONSUMPTION OF ELECTRODIALYSIS.</u>	47
A. Introduction.	47
B. Electrode potentials.	48
C. Voltage drops caused by Ohmic resistance.	53
D. Voltage drops at the membranes.	56
E. Summary.	56
F. The quantity of charge passed through in electrodialytic desalting.	56
G. Calculation of energy consumption and the desalting effect for the electrodialytic desalting of water from experimental data.	57

	pg.
V. CHARGE EFFICIENCY.	63
A. Introduction.	63
B. Definitions of the various efficiencies.	63
C. Derivation of a general expression for current density of an ion in a system of a number of ions in the case of charged membranes.	66
D. A simple calculation of the current density efficiency of an ion present in a system of a number of ions in the case of non-selective membranes.	70
E. Calculation of the charge efficiency of the chloride ion in the cathodic and the anodic membranes from experimental data of electro(dia)lytic desalting experiments of water.	74
F. Charge efficiencies and current efficiencies found in literature.	76
VI. THE EXPERIMENTAL RESEARCH INTO WATER DESALTING.	79
A. Description of the apparatus.	79
B. Experiments with non- or only slightly selective membranes.	81
C. Research into the usefulness of selective membranes for electrodialytic desalting of water.	88
D. Tentative experiments on chloride removal at the anode in a two-compartment cell with non-reversible electrodes.	93
E. Several desalting experiments on potassium chloride solutions in a two-compartment cell with reversible silver-silverchloride-electrodes.	94
F. Discussion of the results.	97
BRIEF SUMMARY.	105
REFERENCES.	107
Tables	I - XVII incl.
Graphs	1 - 18 incl.
Figures	1 - 6 incl.
Appendices	1 - 10 incl.

List of symbols and units

In the text of this report in general no explanation of the symbols used is given. Their meaning can be looked up in this list. In a few cases it was unavoidable to use the same symbols for different items. At such places a supplementary explanation is given in the text and the same applies to the units. Wherever in the text of this report no special units are given all the quantities are expressed in the units listed here.

<u>Symbol</u>	<u>Unit</u>
D	$\text{cm}^2/\text{sec.}$
E	volts
$\frac{dE}{dx}$	volts/cm
F	coulombs/gram equiv.
I	ampères
M	-
N_E	kWh/m^3
O	cm^2
P	g equiv. per cm^2 per sec.
Q	Coulombs
R	ohms
R	(joules per degree C (per mole
T	hours
U	(cm^2 per ohm per (gram-equiv.
V	cm^2 per ohm per gram equiv.
V	litres
W	kWh/m^3
$W(c_p, c_k)$	kWh/m^3

- 11 -

a	Concentration within the membrane pores	g equiv./cm ³
c	Concentration in the free solution	g equiv./cm ³
d	Current density, calculated per cm ² membrane area	ampères/cm ²
i	Current density in the solution	ampères/cm ²
m	Ratio of concentrations in the analyte (cf. Aten (31))	-
n	Transference number	-
n _m	Idem in the membrane	-
n _{cm}	Idem in the cathodic membrane	-
n _{am}	Idem in the anodic membrane	-
P	Ratio of concentrations in the catholyte (cf. Aten (31))	-
q	Desalting effect	g NaCl per 100 amp.hr
q(c _p , c _k)	Average desalting effect during desalting from c _p to c _k m equiv. Cl ⁻ /l	g NaCl per 100 amp.hr
r	Donnan concentration ratio (cf Teorell (90))	sec.
t	Time	cm ² volt ⁻¹ sec ⁻¹
u	Electrolytic mobility of cations	cm ² volt ⁻¹ sec ⁻¹
v	Electrolytic mobility of anions	cm ² volt ⁻¹ sec ⁻¹
w	Energy consumption	watt sec per cm ³
x	Coordinate of length.	cm
y	Concentration in electric units	coulombs per cm ³
z	Thickness of membrane	cm
ζ	Plancks variable (cf Teorell (90) p. 461)	-
η^i	Current density efficiency	-
η^I	Current efficiency	-
χ	Specific conductance	Ω^{-1} cm ⁻¹
ρ	Specific resistance	Ω cm
τ	Absolute temperature	degrees Kelvin
φ	Average charge efficiency for the time interval (0, t)	
ω \bar{x}	Density of the fixed membrane charges, g equiv. per cm ³ expressed as concentration	

- 13 -

The indices + and -, e.g. c^+ , c^- , i^+ , indicate that the symbols apply to the cations or to the anions. The indices ', " and "", show that the indexed symbols relate to different types of ions; symbols without these indices relate to the whole (the total concentration $c = c' + c'' + c''' \dots$). The indices 1 and 2 indicate the two sides of the membrane. Thus, c_1' is the concentration of a certain cation in the free solution on one side, c_2' that on the other side of the membrane.

- 15 -

I. STARTING POINT OF THE INVESTIGATIONS.

Because of the difficulties occurring in obtaining water supplies for domestic, industrial and agricultural purposes, considerable attention is devoted to the desalting of water (1,8,15,24,99).

This applies in the first place to countries where the supply of drinking water is already an important problem or will be within a measurable time (1, 2, 3, 4). In this respect for instance there might be mentioned the Netherlands, the United States and islands such as Aruba and Curaçao (on these islands practically all drinking water has to be prepared in a more or less complex and expensive manner, for instance by distilling sea water, or by obtaining supplies from elsewhere).

Furthermore, the supply of water for irrigation purposes is of great agricultural importance. In the first place we have in mind countries in which it is desired to start reclaiming deserts: Israel, Irak, Persia.

The Netherlands' future supplies of drinking water are endangered by a steady increase in the salinity of underground water caused by the continuous penetration of sea water (displacement of the so-called "salt water boundary" eastwards) and by the discharging of waste water rich in ions by industry, while - owing to the continuous growth in population, the higher standard of living and increasing industrialisation - the water supplies formed by precipitation are failing to meet requirements.

Fig. 1 (5) gives an idea of the fresh water layer floating on sea water, the boundary of which is constantly shifting inland.

In a summary of present and possible future water supplies in the Netherlands (6) it is stated that the amount of water which, as estimated, will be required by the year A.D. 2000 is $890,000 \text{ m}^3/\text{day}$, whilst the amount of water available is:

from the dunes	$113,500 \text{ m}^3/\text{day}$
from other underground sources	$227,000 \text{ m}^3/\text{day}$
total water available approx.	$400,000 \text{ m}^3/\text{day}$

The deficiency will have to be made up by surface water and desalinated brackish and/or sea water.

Salinity in the North Holland polder and polder basin area is already 500-1000 mg chloride per litre, whilst the criteria for fresh, brackish and salt water according to Krul and Liefrinck (6) are:

fresh water	up to 100	mg chloride per litre,
brackish water	100 - 1000	" " " "
salt water	over 1000	" " " "

The salinity of agricultural water must not exceed 300 mg chloride per litre. The water of the North Sea Canal near IJmuiden is salty, while its salinity gradually decreases towards Amsterdam. That of the New Waterway and of the New Maas between Rotterdam and Hook of Holland varies according to the tides and the run off of the river Rhine.

The increasing salinity of polder basin and river water in the Netherlands is becoming serious and occurs primarily in the West of the country (7).

Owing to the great problems arising from the penetration of salt in polder basin and river water in this country, the Research Institute for Public Health Engineering T.N.O. approached the Plastics Research Institute T.N.O. on the question whether it was possible to formulate a process for large-scale desalting sea water or brackish water by ion exchanger treatment.

In reply to this question the Plastics Research Institute T.N.O. issued a report (K.I. 49/151, dated September 14th, 1949) from which it appeared that in the production of large quantities of drinking water from saline river water by ion exchange in most cases, the cost of regenerating the exchangers, even if effected electrolytically, would make the price of the water rather high.

Arising from the conclusions in this report and owing to the fact that the General Technical Department T.N.O. was undertaking extensive research into the electrodialytic desalting of various liquids, this Department was requested on January 20th, 1950 by the Committee for Hydrological Research T.N.O. through the Research Institute for Public Health Engineering T.N.O. to examine the possibilities of electrodialytic desalting of brackish and sea water.

In the countries referred to on page 15 there is of course

also great interest in processes enabling efficient large-scale reduction of the salt content of 18,000 mg Cl⁻/l (sea water) respectively 1,000 mg Cl⁻/l (brackish water) to about 300 mg Cl⁻/l.

II. GENERAL METHODS OF DESALTING WATER¹⁾.

A. Desalting methods for sea water.

Various methods of desalting sea water for domestic use are known. The most important methods are mentioned in Table I with a note of the cost found in the literature (1, 2, 8).

The average rate for water for industrial purposes in the United States is fl. 0.10 to fl. 0.12 per m³, and for smaller quantities (for instance for domestic use) fl. 0.25 per m³. Water for agricultural purposes has, of course, to be much cheaper.

It will be clear that the desalting problem for any particular region is not solved until a method is found which can be economically justified. Therefore the cost per m³ reclaimed water must be calculated separately for each process and for each location.

1. Distillation processes²⁾.

a. Distillation under atmospheric pressure.

The production of drinking water from sea water by means of distillation is applied fairly generally; during the Second World War the United States in this way daily produced water for 1,000,000 people.

By distilling 1.25 kg of sea water one obtains 1 kg of drinking water and 0.25 kg of brine.

The possibility of reaching high efficiency of heat recovery by employing vapour compression has been known

¹⁾ The patent literature was reviewed by the Patents Department T.N.O. Appendix 1 lists patents in the United States, Great Britain, Germany, France, Switzerland, the Netherlands up to 1951 in the class 85 b 1 (processes for the purification of water for industrial use and of drinking water), distillation processes excepted.

²⁾ Appendix 2 lists the numbers of patents up to 1950 in the class 12 a 3 a (distillation processes) relating to desalting of water.

for some time, but was not generally applied until the Second World War. The considerable saving obtained in operating costs by applying vapour compression as compared with the outmoded distillation methods is clearly shown in Table II.

At present it is possible to produce 175 to 200 kg of water with the aid of 1 kg of fuel by means of this process (1, 8). Leicester (8) calculated that the maximum water-to-fuel ratio is 270 : 1.

According to Latham (10) it thus appears very unlikely that cost of distillation can be reduced to less than half the present cost if the cost of fuel remains about the same.

Systems which in one way or another make use of solar energy are of course not restricted to this ratio of 270 : 1. In the Virgin-islands for instance, 3.8 m³ per day is prepared through distillation with solar energy (see also (9)).

Power and depreciation are the predominant items in the total production cost of a vapour compression still (Graph 1). For this reason distillation is attractive in places where fuel can be obtained at very low cost (oil wells; natural gas deposits). The biggest sea water distillation installation is that built by the Kuwait Oil Co. in the Persian gulf (capacity 2600 m³/day). This installation is associated with oil development and presumably uses refinery wastes for fuel (2).

The distillation of sea water is also applied extensively in Aruba and Curacao (11).

The size of the vapour compression distilling plant compares very favourably with that of the conventional evaporator. The overall size of a typical commercial unit, designed for an output of 25,400 kg water/day is 2.7 x 1.7 x 1.8 m (weight 5600 kg).

Therefore the compression still can also be used instead of stored water on diesel and petrol engine-propelled ships, which will release valuable space for cargo or fuel with a corresponding increase in the ship's cruising radius.

As regards the use of atomic energy for distillation Dubridge

(12) says that thirty to fifty years will elapse before uranium can possibly become a major source of power and that this power will certainly cost much more than power from coal. It will be advisable to watch developments in this respect.

b. High-pressure distillation.

In 1950 Von Platen (13) developed a process for separating dissolved salts from their solvent with a very small amount of energy, which is especially suited for the production of drinking water from sea water.

If sea water is subjected to distillation at a pressure far above the critical value for water, say 300 to 360 kg/cm², a modest-sized heat exchanger will do in transmitting practically all the heat of condensation to the sea water feed, thus giving a low fuel ratio.

This process can also be used for preparing drinking water on board ocean-going ships. No cost evaluation is given. Von Platen shows thermodynamically that it does make a considerable difference whether one works at or well above critical pressure.

2. Desalting by freezing out.

With freezing out the quantity of "heat" used is less than with distillation; on the other hand, however, "heat-calories" are cheaper than "cold-calories", and therefore these processes should again be compared for each location.

There are three methods of freezing out sea water of which Steinbach gives a review without, however, stating the cost (14). Salt concentrations of 0.14 per cent can be attained.

Aultman (1) points out that freezing out sea water would probably cost at least Fl. 1.25 per m³.

3. Desalting by ion-exchange.

The "mixed bed" demineralisation-process was originally suggested by Akeroyd and Kressmann (15) for desalting sea water in case of emergency, for instance in wartime. "Mixed bed" demineralisation units were used in fairly large quantities during the latter part of World

War II by the R.A.F. Furthermore, they were occasionally used in sea-going vessels.

However, an expense which is permissible in wartime is not usually accepted in peace time. The unit cost of the process is directly proportional to the salinity of the water being demineralised and is rather high in the case of sea water. (In South California the chemicals cost only is estimated to be Fl. 25.-/m³).

As it requires twenty to thirty times the amount of demineralised water produced just to wash the regenerating acid an alkali from the demineralising material, this process is unattractive from an economical point of view. According to Aultman (1) and Moore (99) the economic limit of the present process is reached when the raw water contains 2000-2500 mg/l total salines, less than one-tenth the salt content of sea water. According to Showell (16) the cost of ion exchange is uneconomical compared to distillation for concentrations above 1500-2000 mg/l solids.

4. Electrolytic desalting¹⁾.

This paragraph deals with the systems which use electric power for desalting sea water.

a. Electrolysis of sea water utilizing one diaphragm.

Electrolysis of sea water using one diaphragm is in use for production of caustic soda and/or chlorine, sterilization of sea water, but not for desalting purposes. It will be quite obvious that the anode and the diaphragm are very liable to corrosion.

According to Inoue (17) in the production of caustic soda a moulded anode made of a mixture of lead dust and powdered graphite in 7.5 - 15:1 ratio appeared to resist corrosion the best. A typical process for producing caustic soda from sea water owes its effectiveness to the use of asbestos diaphragms (18). Nishida and co-

¹⁾ Appendices 3, 4 and 5 respectively list patents up to 1950 in the classes 12 h 5 (electro-osmosis), 12 h 3 (diaphragms for electrolytic purposes in general), and in 12 d 1 d (clarifying and separating liquids by electrical action) and 12 h 1 (electrolytic processes and equipment in general).

workers (19) use diaphragms of ion exchange resin (i.e. melamine resin) to prevent the moving of hydroxyl ions produced around the cathode towards the anodic compartment.

Electrolysis of sea water is also employed for its bacteriological purification as such electrolytic chlorination can kill all living organisms and is more satisfactory in this respect than dosing with hypochlorite or chlorite solutions (21). A Gloucester fish plant employs a simple electrolytic unit to generate chlorine in harbour water. After dilution (120 mg/l of free chlorine to 15 mg/l) the latter is then used to wash all incoming fish, floors, walls and equipment (20). Prime benefits are: reduction in bacteria counts on the fish and subsequent improvement in keeping quality of the fillets, decrease in objectionable "fishy" odours about the plant, and elimination of slime from the various working surfaces.

Carbon or graphite-amalgam electrodes are used ($\delta = 1.9$; $O = 45 \text{ dm}^2$; $I = 75$; $V = 9.75$; $d = \pm 17 \text{ mA/cm}^2$; energy consumption 3 kWh¹) which must be replaced about once a year. Cost of replacement is approximately Fl. 247.- per electrode. At a capacity of the entire unit of 11 m³ water of 120 mg free chlorine per litre per hour the power cost, at Fl. 0.075 per kWh, is Fl. 0.225 per hour. A portable chlorine generating unit has been designed for processing fresh water or water with a low salt content, especially suitable for use in fruit and vegetable canneries.

A computation of power for these electrolytic processes with one diaphragm is found only in Aultman's article (1). If the electrolytic process developed by Briggs (22, 23) which is used for boiler water treatment, were to be used for treating sea water, the cost for power alone would be Fl. 0.90/m³ at Fl. 0.02 per kWh. Furthermore this method would require a water waste of four times the recovery.

¹) Explanation of the symbols cf. pg. 9.

b. Electrodialysis.

Electrodialysis has been known for some time and, as appears from the literature in this field, has been fairly extensively investigated, at least as regards its application on a laboratory scale.

Electrodialysis should be looked upon as a combination of dialysis and electrolysis: in electrodialysis the diffusion of ions through the membrane is influenced in part by the electric field; colloidal solutions for instance can be freed of dissolved salts more quickly with the aid of electrodialysis than of ordinary dialysis.

Electrodialysis was first applied on an industrial scale about 1925 in the elektrodialytic production of "distilled" water (see sections III.B and C), while in 1951 industrial electrodialytic desalting of milk-whey materialised.

A method for the technical demineralisation of sea water by electrodialysis with new synthetic membranes, the so-called Permionic membranes, has been announced by the Ionics Incorporated (24, 25, 26). 1.5 m³ sea water yields 1 m³ purified water and 0.5 m³ brine.

At a comparatively low flow rate of the sea water the energy consumption can be as low as 5.2 kWh/m³. As to the cost of the equipment: the apparatus has no moving parts other than the water stream; water pumping costs are negligible; the process is continuous and uses no heat or chemicals. Therefore at a kWh rate of Fl. 0.04 the total cost is estimated at Fl. 0.30 to Fl. 0.35 per m³, which is one half to one third of that required by the most economical process now commercially available: the vapour compression distillation.

Since the membranes are quickly affected in electrodialysis of water containing chloride ions they will have to be replaced regularly. This cost of replacement may be considerable and has very probably been left out of account in calculating the so-called "total" cost and therefore this total cost is probably nothing but the operating cost.

From the summary given by Aultman of present known methods of sea water desalting he concludes that for the time being the cost will be at least twelve to more than five hundred times as much as the average for existing supplies. According to this author from an engineering standpoint there is - within the foreseeable future and in the light of current technical knowledge - no question of sea water being considered as a source of domestic, industrial or agricultural water along either coast of the U.S.A. or of local water supplies in general being superseded by the ocean. He would rather make every effort to improve and develop existing local supplies: treating of sewage and industrial wastes, better rainfall collection.

At places where supplies of potable water are not available and water is vitally needed now, a choice should however be made of the reviewed desalting methods of either sea water or brackish water. Research into these methods should therefore be encouraged. Which method is most economical depends upon the salinity of the water to be treated and the form of energy available.

B. The desalting of brackish waters.

Water is brackish when it has been contaminated with moderate salt concentrations (1/10 to 1/5 that of sea water) by intrusion of sea water or oil brines into fresh well water or by percolation of fresh water through rocks and soils containing soluble minerals. According to Krul and Liefrinck (6) the criteria for fresh, brackish and salt water are:

fresh water	up to 100 mg Cl ⁻ /l
brackish water	100 - 1000 mg Cl ⁻ /l
salt water	over 1000 mg Cl ⁻ /l

Brackish waters are now widely found in the Western States of the U.S.A., Bermuda, The Hawaiian Islands, the Bahamas, Cuba, in certain regions of Europe and in many desert areas of Asia, Africa and the Middle East.

In principle all the methods mentioned in A can be used for desalting brackish water.

1. Distillation.

Because of the lower concentration of solids, process costs will be somewhat lower than those for seawater (section II.A.1).

2. Ion-exchange.

Owing to the lower salinity of the starting liquid, ion exchange is more favourable in this case. Some examples on this subject now follow.

From the results of extensive research into ion exchange for water treatment by Showell (16) it is clear that for reducing a solids content of water of 250 mg/l demineralisation is cheaper than vapour compression distillation. Typical values given for operation cost of a 1000 l/min. capacity compression still, ordinary still and demineralisation plant are Fl. 1.48, 1.81 and 0.44 per m³ respectively. In comparison with these prices chemical softening is so far less expensive (16).

According to Juda the cost of the Ionics partial demineralisation process for desalting brackish water from \pm 1,000 mg Cl⁻/l to \pm 300 mg Cl⁻/l is Fl. 0.145/m³¹). In this process regeneration is carried out with sulphuric acid and lime, the prices of which are Fl. 10.- and Fl. 5.- per 100 kg respectively.

Aultman (1) quotes a cost¹) of Fl. 0.265/m³ for the production of water equal in quality to distilled water from raw water containing about 370 mg/l total dissolved solids.

At the central power station at Villers-Saint Paul (Fr.) 90,000 m³ water per hour from the Oise is demineralised by cation-anion-exchange (27).

At present research into the possibility of desalting water in Holland by means of ion exchangers still carried out by the Plastics Research Institute T.N.O.

3. Electrodialysis.

As electrodialytic desalting of water is the subject of this

¹) No further details of this cost are given and it is not known whether it is the total cost or cost of chemicals only.

report, the electrodialytic desalting experiments already made with brackish waters, will be discussed in detail in a separate section (see section III).

4. Electrolysis.

In a two-compartment cell, using one diaphragm, Briggs (22, 23) produces soft water at lower power cost and with a lower percentage of waste water than has formerly been possible with the three-compartment cell used by the Siemens and Halske A.G.

The energy consumption for decreasing the solids content of 770 mg/l to 500 mg/l is 1.1 kWh per m³.

III. ELECTRODIALYTIC REMOVAL OF SALTS FROM BRACKISH AND SIMILAR WATERS.

A. Introduction.

The principle of desalting by means of electrodialysis is that cations and anions are removed from the dialysate via two or more membranes under the influence of an electrical field.

At the cathode lye and hydrogen are formed; the hydroxyl ions then move in the direction of the anode. At the anode acid and oxygen are formed. The anodic hydrogen ions are responsible for a decline in the pH of the anolyte and move towards the cathode. The phenomena occurring in the presence of halogens are extensively dealt with in section III F.

Hence, when two not fully selective membranes are used, in the absence of stirring the pH of the dialysate will show a decline from high at the cathodic membrane to low at the anodic membrane. Intensive stirring will cause the hydrogen ions and the hydroxyl ions to combine into water molecules so that the pH will remain constant, if as many hydrogen ions as hydroxyl ions enter into the dialysate. This is not the case, however. If membranes are used which are equally permeable for both the aforementioned ions more hydrogen ions than hydroxyl ions will enter the dialysate, since the mobility of the hydrogen ion exceeds that of the hydroxyl ion. This is evident from Table III which shows the mobilities of different ions at 25°C. In the absence of special measures the dialysate is therefore diluted somewhat and its pH falls. According to Billiter (29) the dilution effect, when water is desalinated, is very slight, viz., 0.03%.

As variation in the pH is undesirable, particularly when colloidal solutions are desalinated (denaturation), efforts have been made to obviate this by the use of selective membranes, and much research has been performed in this field.

At the same time it is obvious that when less-selective membranes are used a large proportion (according to Billiter: 80%) of the current transport is supplied by the hydroxyl ions and by

the hydrogen ions passing towards the anode or the cathode. Not until 1939 did Manegold (30) clearly establish the correlation between the use of selective membranes and the efficiency of the desalting process. By means of calculations he proves that all the current transport is supplied by the ions to be removed from the dialysate if membranes are used, in which the charge efficiency (definition see section V B) of the anion or cation to be concerned is 100% (see Fig. 2b). In this case both the anolyte and the catholyte may be concentrated electrolytic solutions, as a result of which the energy consumption will be substantially reduced. It is to be expected that the energy cost of electrodialytic desalting will become lower if the charge efficiencies of the salt ions to be removed are as high as possible in the membrane(s) in question.

If in the aforementioned case the membranes are interchanged, then the electrolyte will accumulate in the middle cell (see Fig. 2c).

The result of the use of a number of membranes is shown diagrammatically in Fig. 3. The electrolyte becomes concentrated in alternate cells.

Aten (31) has calculated that, if all compartments of the three-compartment electrodialysis cell are filled with the same solution, desalting of the dialysate is possible by using either selective membranes or two identical membranes. In the latter case the degree of acidity or alkalinity of the anolyte or the catholyte should be of a specific value. The maximum "current efficiency" attainable (see section V F) is then only 20%, whereas in the other case this maximum value depends upon the selectivity of the membrane, and may be higher.

For further details and the history of electrodialytic desalting we may refer to the publications of Stamberger (32), Stauffer (33) and of Prausnitz and Reitstötter (34).

In the next pages we will give a survey of some important electrodialytical water desalting experiments known from literature. Next the above mentioned theoretical computations by Aten will be reviewed, whereafter a brief survey of the electrode processes occurring at the electrodes during electrodialytic desalting of water containing chloride ions will be given.

B. The principal patents relating to electrodialytic desalting of water¹⁾.

The use of electrodialysis for water purification is a special feature of the patents of the Elektro Osmose Gesellschaft and of the Siemens & Halske A.G. (35). However, direct conclusions regarding the problems related to the desalting of sea water and water with 1000 mg Cl⁻/l are not given. On the other hand, they do contain some data which might provide a starting point. An example is given of the desalting of water from 35 mg Cl⁻/l to 10 mg Cl⁻/l in the normal three-compartment cell, with an energy consumption of 13.2 kWh per m³. In addition there are other data which relate to the elimination of bicarbonate etc. Briefly this procedure comes to the addition of the spent rinsing liquids to the water to be desalinated, whereupon owing to their alkalinity they will precipitate the bicarbonate in the form of carbonate.

An important feature of all these patents is the aim of limiting the distance between the electrodes. Attention is also paid to the pH regulation. For this purpose systems are indicated which involve mixing of the cathodic and anodic rinsing liquids.

A Dutch patent, (cf. (36)) in the name of J. Billiter, is also of importance in this investigation. He suggests to reduce the back-flow of water of a low salt content towards compartments with water of a high salt content by maintaining a hydrostatic pressure difference and by means of a correct choice of diaphragms. In the case of porous clay diaphragms, where the osmotic transport of water through the membranes is about one hundred times as much as the H⁺ + OH⁻ → H₂O quantity (see pg. 27) it is clear that this transport can be quite considerable.

When desalting liquids of a high salt content is concerned and untreated water is used as rinsing liquid a substantial difference in concentration will arise between dialysate and rinsing liquid.

¹⁾ The patents referred to here are also mentioned in appendices 3, 4 and 5.

Consequently:

- a. a higher hydrostatic pressure difference is necessary to prevent undesirable water transport.
- b. a higher current density is necessary to suppress undesirable dialytic salt transport.

In many cases the maintenance of a very large pressure difference is needed, for instance by working with nearly empty electrode compartments. The electrodes are then placed right against the diaphragm. Asbestos and ceramics are suggested as suitable materials for the diaphragms, since they are chlorine-resistant. The results of some of Billiter's experiments are listed in Table V. The Siemens & Halske A.G. later on also suggests the application of a pressure difference (D.R.P.498,048, cf (35)).

C. Brief survey of the literature on the electrodialytic water desalting.

A survey of the demineralisation of water by electrodialysis is given by Illig (37) and by Prausnitz and Reitstötter (34). Like in the case of sea water germicidal properties are attributed to electro-lytical chlorination (e.g. (31), (34)), whereas according to Prausnitz and Reitstötter (34) water can be more thoroughly purified by means of electrodialysis than by distillation. A review is given of the investigations of Siemens, Billiter, Zhukov and Juda, as published in the literature.

1. The investigations of Siemens and Halske A.G.

The electrodialytic elimination of salts from water in the three-compartment cell has been developed on a laboratory scale and subsequently on a technical scale mainly by the Siemens and Halske A.G. (cf Illig (38) and Gerth (39)). Apparatuses were constructed with a capacity of 20-5000 l/day for the preparation of various qualities of softened water. The water to be desalinated flowed through consecutive middle compartments, rinsing being done with untreated water. For the preparation of highly purified

water the last cells had to be rinsed with distilled water.

Various membranes were used. Vegetable fibre (e.g. "Kuttertuch") proved satisfactory as material for the cathodic membrane and animal fibre for the anodic membrane (e.g. specially treated leather, "Vulkanfiber" or wool with chrome gelatine). Experiments have also been performed with microporous rubber. However, various difficulties arose, owing to corrosion of the anodic membrane as soon as the water contained chloride ions (e.g. (31)).

The apparatuses of Siemens have also been described by many other investigators, viz. in Germany (40-44), France (45, 46, 47)), Britain (48, 49, 50) and in the Netherlands (51), where Aten (31) made a special study of the electrodialytic purification of water from the river Vecht with the aid of Siemens' apparatus. Generally speaking these articles contain no data other than those already referred to the publications of Illig (38) and Gerth (39). Bartow (50) carried out research into various conditions and observed that time and energy are lost when switching on, as it takes one hour before suitable water is obtained.

The energy consumption depends upon the salt content of the water and the degree of purity desired. According to Behrmann (49) the process is no longer economical if the total solids content is higher than 1000 mg/l. Water for breweries which has to be only partly purified, requires 10 kWh/m³ (42), whereas otherwise in the literature values are found varying between 15 and 50 kWh/m³. Sarrot (45) arrives at an energy consumption of 20-25 kWh/m³ for a desalting from 250-300 mg solids/l to 0 mg/l and remarks that this figure can be considerably reduced if a total solids content of 30-40 mg/l is permissible.

The flow rate of the dialysate can be varied only within certain limits (41). Bartow (48) reports a rate of 24, Aten one of 3.6 l/h. With Bartow the flow rate of the rinsing water was between the limits of 12 and 49 l/h, whilst in Aten's case it was $\frac{1}{2}$ l/h in the first eight and 0.12 l/h in the last two cells. The amount of rinsing water to be used varies considerably for the different investigators, viz. from $\frac{1}{2}$ - $1\frac{1}{2}$ times the production to 3 - 4 times the production.

The current density applied by Aten was 1 ma/cm².
Patin (46) fills the apparatus with four litres of water and after one hour determines the water and energy consumption, the acidity of the anodic and the alkalinity of the cathodic liquid, the conductivity, the pH (dropped to 6) and the temperature (increased by 2 - 3°C).

2. Billiter's method.

Billiter regards the desalting process during the electrodialysis in a three-compartment cell with neutral membranes as a substitution of the salt ions by hydrogen ions and hydroxyl ions. According to him the fewer foreign cations are contained in the anolyte beside hydrogen ions, and the fewer foreign anions are contained in the catholyte beside hydroxyl ions, the better the "current yield" (see section V.F) will be. It attains a maximal value when the anolyte is a pure acid and the catholyte a pure alkali. However, in that case the formation of acid in the dialysate is likewise maximal.

These claims are confirmed by the results of desalting experiments of various natural as well as artificially salted waters, ranging in salt content from 50 to 5000 mg/l (29). In these experiments the middle compartment and the cathodic compartment contained the non-treated water and the anodic compartment a diluted acid, viz., 0.001 n sulphuric acid.

The cathodic diaphragms were usually made of closely woven cotton filter cloths, except when the water contained relatively high concentrations of alkali salts and experiments extended over a long period, then asbestos diaphragms being used instead. The anodic diaphragms consisted of porous clay cells with a wall thickness of 5 mm which possessed a small negative charge.

The potentials applied were 440, 220, 110, 64 and 12 volts. During the course of the electrodialysis, which was continued day and night without interruption, the acid concentration of the anolyte gradually increased, more rapidly when the untreated water contained sulphates. In many cases the acid concentration rose to 0.1 n. However, he could not observe any effect on the "current efficiency" within this range of acidity, provided there was no defect in the diaphragm. He found a "current efficiency" of 16-18% for the complete desalting of waters

in the middle compartment, with salt contents of 160, 341 and 642 mg/l.

For details of his experiments and the apparatus we refer to the article of Billiter itself (29).

The principal conclusions of his investigations are:

- a. the liquid transported by electro-osmosis through the anodic diaphragm is pure or almost pure water.
- b. natural water can be almost completely desalinated, even when a relatively concentrated acid solution is used as anolyte.
- c. no desalting of the water in the middle compartment takes place if the anolyte and catholyte are maintained neutral.
- d. the sign or size of the static potential of the diaphragm charge has no noticeable effect on the output of the cells. (in other words: a greater variety of anodic membrane material!).

According to Billiter, therefore, the flushing of the two outer compartments, as has been done by the Siemens and Halske A.G., is unnecessary providing perfect diaphragms are employed. Even omitting the flushing of one of the cell compartments means a decided simplification in cell design. The energy consumption for complete desalting equals $0.0023 V \cdot s \cdot \text{kWh/m}^3$ (V = average voltage of the cells in volts; s = salt content of the untreated water in mg/l). By application of this equation to our desalting range (1000 mg Cl⁻/l - 300 mg Cl⁻/l) it would be approx. $V \times 3.8 \text{ kWh/m}^3$.

For the treatment of waters with a high salt content the operating costs of his cells can be appreciably reduced if the untreated water is first given a chemical treatment with zeolites, before being fed into the cells. Thus, for example, the salt content of the water can be reduced from approx. 30,000 mg/l down to 400-500 mg/l before feeding into the electrodialysis cells.

3. The investigations of Zhukov.

Zhukov (52) purifies water from the river Neva by electrodialysis

in a three-compartment cell, as used by Billiter, equipped with two unequal negatively charged diaphragms. The latter are characterized by the following porosity, mean pore diametre, transference number of the chloride ion in 0.01 n potassium chloride, electrokinetic potential:

anodic (grog, 1200°) 0.28, 4.08 μ , 0.504 and 15.1 m v
cathodic (clay, 800°) 0.35, 0.04 μ , 0.341 and 7.3 m v

At a current density of 1-5 mA/cm² and a flow rate of 3 l/h the energy consumption to obtain water with a dry residue of 10-12 mg/l and an ignition residue of 6-8 mg/l is 12-14 kWh/m³. The salt content of the non-treated water is not mentioned. After pre-filtering through sand (5 cm thick) it was possible to increase the flow rate to 5 l/h, as a result of which the energy consumption fell to 8 kWh/m³.

The anodic diaphragm is regenerated by a 1% solution of caustic soda at 50°C, preferably after passing 350-400 l of water. With water pre-filtered through sand and active coal, the lifetime of the anodic diaphragm is two to three times longer. The cathodic diaphragm requires only scraping of an 0.5 mm thin peptized layer after prolonged use.

In the same apparatus he has determined the "current efficiency" for the calcium ion and the sulphate ion in a 0.01 n calcium sulphate solution (see section V.P.).

Zhukov (52) stresses the fact that when selecting the rinsing rate of the catholyte one should allow for the fact that at higher lye concentrations there may arise not only an increase in energy consumption but also changes in the transference numbers of the ions in the cathodic membrane. In one experiment the transference number of the chloride ion dropped from the initial value of 0.343 (in 0.01 n KCl) to 0.27.

4. The use of Permionic membranes.

The new Permionic membranes (24), used for the desalting of sea water can also be used in the purification of many common brackish waters with a salt content of 3600 mg/l and lower. Juda (24) states that in these cases the energy costs will amount to Fl. 0.01 per m³, for a kWh-price of 1 Dutch cent. Energy consumption is therefore approx. 1 kWh/m³. However he did not take into account the renewing costs of the membranes (see remark section II A.4.b).

D. Review of the theoretical computations by Aten in the electro-dialytic desalting of water in a three-compartment cell.

Aten (31) considers the situation in a three-compartment electro-dialysis cell as used by the Siemens & Halske A.G., all compartments being continuously fed with raw water.

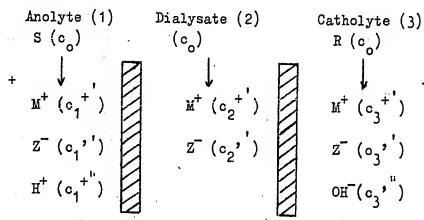
Neglecting the diffusion and the transport of water through the membranes, he arrives at the following conclusions by means of calculation:

1. If the mobilities of the anions and the cations in both diaphragms are equal or proportional to the mobilities of these ions in the free solution, desalting is possible only if the anodic and the cathodic rinsing liquids possess the correct degree of acidity and alkalinity.
2. Desalting of water with neutral raw water flowing into all three compartments can be achieved only by the correct use of selective membranes.

1. Desalting with non-selective membranes.

If two identical membranes are situated between the three compartments filled with salt (MZ) containing water, the middle compartment can nevertheless be desalinated if by carefully regulating the rinsing rates one ensures that the anolyte and the catholyte possess the right degree of acidity or alkalinity and the middle compartment remains neutral.

Neglecting the number of hydrogen ions and hydroxyl ions in water the "stationary state" may be represented as follows ¹⁾:



When the assumption is made that $u' = v'$, $u'' = 5 u'$ and $v'' = 3 u'$, and in addition the factors m and p are introduced, of which $m = c_1^+ / c_1^{'}$ and $p = c_3^+ / c_3^{'}$, the following equations can be derived:

$$m = \frac{4p-1}{4+p} \quad \text{and} \quad p = \frac{4m-1}{4-m}.$$

The reduction of the amount of the salt MZ in the stationary state is given by:

$$P = \frac{d}{F} \cdot \frac{1-p}{5p-2} \text{ g eq/cm}^2 \text{ sec}$$

P is negative, i.e. the salinity in the middle compartment decreases, if p is > 1 , in other words if the catholyte is alkaline.

The quantity

$$-\frac{1-p}{5p-2} = -\frac{PF}{d} \text{ (g eq)}$$

indicates the amount of salt which during the passage of 1 Faraday is removed from the middle compartment. The maximum value is 0.2 (when p is 0) and so the maximum "current efficiency" is 20% (cf. section V F).

¹⁾ in parenthesis the ion concentrations are given in g eq per cm^3 .

In section IV F we qualify the desalting effect by the quantity q : the number of grammes of sodium chloride removed from the middle compartment per 100 ampère-hours. In connection with the above equation q cannot exceed the value of $0.2 \times 218.4 = 43.6$.

From the equation for P it is evident that the absolute concentrations of acid and alkali in the electrode compartments and the salt concentration in the middle compartment exert no influence, but that desalting depends exclusively on the relative alkalinity and acidity of the catholyte and the anolyte, viz.

$$\frac{c_1^+}{c_0} = \frac{m+1}{2m} \quad \text{and} \quad \frac{c_3^+}{c_0} = \frac{p+1}{2p}$$

In order to obtain the desired ratio $\frac{\text{acidity}}{\text{alkalinity}}$ the rinsing liquids have to be given a certain flow rate. If A represents the flow rate in cm^3 per sec. per cm^2 diaphragm of the anolyte, B that of the catholyte and c_0 the feed concentration then R and S are given by the equations:

$$A = \frac{d}{F} \cdot \frac{1}{c_0} \cdot \frac{2m}{(6m-4)(m-1)}$$

and

$$B = \frac{d}{F} \cdot \frac{1}{c_0} \cdot \frac{2p}{(4p-2)(p-1)}$$

The only value to be chosen at random is the acidity of the anolyte or the alkalinity of the catholyte. For different values of p , the values for m , q , c_1^+ , c_3^+ and the "current efficiency" can be found in the following table:

p	m	"current ¹⁾ efficiency"	$q^2)$ g NaCl/100 amp.hr.	c_1^+ $\frac{c_1^+}{c_0}$	c_3^+ $\frac{c_3^+}{c_0}$	$c_1^{'}$ $\frac{c_1^{'}}{c_0}$	$c_3^{'}$ $\frac{c_3^{'}}{c_0}$	$\frac{F \cdot c_0}{S \cdot d}$	$\frac{F \cdot c_0}{R \cdot d}$
2	1.5	12.5	27.6	0.83	0.75	0.42	0.75	1.2	0.66
3	1.86	15.4	33.6	0.78	0.67	0.67	1.34	0.60	0.30
4	2.12	16.7	36.6	0.77	0.63	0.83	1.87	0.43	0.19
5	2.33	17.4	37.8	0.72	0.60	0.95	2.40	0.35	0.14
6	2.50	17.8	39.0	0.70	0.58	1.05	2.90	0.30	0.11

¹⁾ maximum possible value 20%

²⁾ maximum possible value 43.6

Hence for the electrodialytic desalting of water containing 1650 mg sodium chloride per litre (= 1000 mg Cl⁻/l) - with the use of a membrane of 500 cm² area and of a current density of 3 ma/cm² - the following combinations and flow rates of the rinsing liquids for the "stationary state" can be calculated for p-values of 2, 4 and 6:

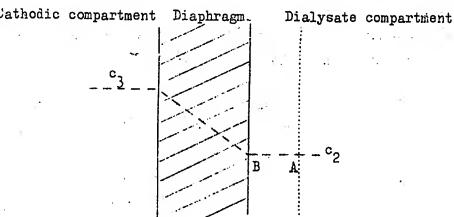
p	Anolyte		Catholyte		q g NaCl/100 amp.hr
	composition	flow rate 1/h	composition	flow rate 1/h	
2	NaCl 0.025 n + HCl 0.013 n	2.2	NaCl 0.023 n + NaOH 0.023 n	1.2	27.6
4	NaCl 0.022 n + HCl 0.025 n	0.8	NaCl 0.019 n + NaOH 0.056 n	0.35	36.6
6	NaCl 0.021 n + HCl 0.032 n	0.55	NaCl 0.017 n + NaOH 0.087 n	0.2	39.0

In the calculations the diffusion and water transport through the membranes have not been taken into account. Yet a certain amount of acid from the anodic compartment and alkali from the cathodic compartment will diffuse towards the dialysate compartment, depending upon the nature of the membrane or the diaphragm and the acid and alkali concentrations. This will determine whether it is more economical to work with larger or smaller values of p and m. When p increases the acid and lye concentrations increase more than q (of the tables). In the case of slight diffusion it is better to work with a large value of p, in the case of considerable diffusion with a small value of p.

If in practice the dialysate compartment becomes acid or alkaline one can slightly reduce the degree of acidity or alkalinity, or increase the flow rates. In any case it will be necessary to investigate by means of experiments, whether the stationary conditions mentioned above and the q values of 28, 37 and 39 can indeed be realised.

2. Desalting with the use of selective membranes.

When the three compartments, filled with salt (M2) containing water, are divided by two diaphragms one of which -e.g. the cathodic- is selective and the current has passed through for some time the salt concentration will drop in the membrane from c₃ g eq/cm³ in the cathodic to c₂ g eq/cm³ in the dialysate compartment.



When A represents a random cross section of the dialysate compartment parallel to the diaphragm, the decrease of the salt concentration in the space between A and B amounts to:

$$P = - 2 \frac{RT}{F} \cdot \frac{c_3 - c_2}{\delta} \cdot n_m^- \cdot u - \frac{d}{F} (n^- - n_m^-) \text{ g eq/cm}^2 \cdot \text{sec.}$$

(n_m⁻ = transference number in the membrane)

In this equation P is maximal if n_m⁻ = 0, i.e., if in the experimental conditions a 100% cation-permeable membrane is used. In that case ($\frac{PF}{d}$)_{max.} then equals n⁻.

The current density must exceed the minimum value (P = 0; q = 0):

$$- d_{\min} = 2 RT \cdot \frac{c_3 - c_2}{\delta} \cdot \frac{n_m^-}{n^- - n_m^-} \cdot u$$

This minimum current density is maximal when $c_2 = 0$, viz.

$$-d_{\min} = 2 R \mathcal{T} \cdot \frac{c_3}{\delta} \cdot \frac{n_m^-}{n^- - n_m^-}$$

Since $\frac{n_m^-}{n^- - n_m^-}$ increases rapidly by an increase of n_m^- , it is advisable to select a diaphragm with a small n_m^- value. At a certain value of n_m^- the necessary current density is lower at greater thickness of the diaphragm and a lower mobility of the M^+ -ion. For small values of n_m^- (say 0.1) desalting is not greatly influenced by the concentration, whether the current density be great or small.

If a number of electrodialysis cells is placed in series the concentration in the first cell will drop from c_3 to c_2 , in the second from c_2 to c_1 , etc. (the concentration of the rinsing water is c_3 throughout). A calculation reveals that -as to the current yield- an apparatus works most economically if the current strength is adjusted to a value rendering zero concentration in the last cell. In this case all cells contribute equally well to the purification.

If S represents the amount of water to be desalinated passing through the middle compartment of a set of 6 electrodialytic cells, expressed in cm^3 per second and per cm^2 diaphragm, he finds the following expression for the current density required

$$-d = \frac{c_3 \cdot S}{6 q} = c_3 \cdot \frac{S \cdot F}{6(n^- - n_m^-)} \text{ amp./cm}^2$$

When as little energy as possible is used for a given quantity of electrolyte, the following ratio should be minimal:

$$\frac{G}{P} = H \cdot \frac{d^2}{P}$$

G = the loss of electric energy per cm^2 diaphragm area,
 H = the electric resistance of the diaphragm, expressed in ohms per cm^2 .¹⁾

¹⁾ Apparently Aten neglects the resistance of the solutions in the respective compartments.

In that case for one diaphragm, say the cathodic diaphragm, the optimum desalting velocity is:

$$P_{\text{opt.}} = \frac{2 R \mathcal{T}}{F} \cdot \frac{c_3 - c_2}{\delta} \cdot n_m^- \cdot u \text{ g eq/cm}^2 \cdot \text{sec}$$

and the corresponding current density:

$$-d_{\text{opt.}} = 4 R \mathcal{T} \cdot \frac{c_3 - c_2}{\delta} \cdot u \cdot \frac{n_m^-}{n^- - n_m^-} \text{ amp./cm}^2$$

Hence it is possible to effect desalting with the use of only one selective diaphragm.

Of course it is more economical to use as well a selecting cathodic as a selective anodic diaphragm. When two equally thick diaphragms are used and the concentrations in the cathodic and anodic compartments are the same, viz. c_3 , the decrease of the salt concentration is represented by the following equation:

$$P = -\frac{2 R \mathcal{T}}{F} \cdot \frac{c_3 - c_2}{\delta} \cdot (u_{\text{cm}}^- \cdot n_{\text{cm}}^- - u_{\text{am}}^- \cdot n_{\text{am}}^-) - \frac{d}{F} \cdot (n_{\text{cm}}^- - n_{\text{am}}^-) \text{ g eq/cm}^2 \cdot \text{sec}^1$$

$$\text{and } q^1) = \frac{n_{\text{cm}}^- - n_{\text{am}}^-}{2} \cdot 218.4 \text{ g NaCl/100 amp.hr}$$

As v for a cathodic and u for an anodic diaphragm have to be small, $n_{\text{cm}}^- - n_{\text{am}}^-$ will be approximately twice as large as $n^- - n_m^-$.

The term for d_{\min} is roughly the same as with one diaphragm.

When desalting is performed with a greater current density, then:

$$P = (d_{\min} - d) \cdot \frac{n_{\text{cm}}^- - n_{\text{am}}^-}{F} \text{ and } q = \frac{d_{\min} - d}{d} \cdot (n_{\text{cm}}^- - n_{\text{am}}^-) \cdot 218.4$$

As compared with the desalting using only one selective diaphragm $n_{\text{cm}}^- - n_{\text{am}}^-$ is approximately twice as large, but d_{\min} remains

¹⁾ n_{cm}^- and n_{am}^- are the 2 transference numbers of the anions in the cathodic membrane and anodic membrane resp.

nearly the same. With the use of one cation- and one anion-permeable diaphragm the degree of desalting therefore will be nearly doubled.

E. The experiments of Hoffmann.

In view of the character of our experimental research the experiments of Hoffmann are briefly reviewed here.

Hoffmann (53) extensively studied the electrodialytic desalting of a 0.88 n sodium sulphate solution, as during electrodialysis of potassium chloride solutions the anodic diaphragm was severely corroded.

Use was made of identical diaphragms of the "Makotuch" type which after two or three day's use were found to have acquired a very limited permeability to water.

The dialysate (1800 cc) was vigorously stirred; the circulating rinsing liquids (totalling 4000 cc distilled water in the anodic and 3250 cc in the cathodic compartment) grew acid resp. alkaline during desalting; the volumes of the three liquids were kept to the mark by replenishing; the distance between the two diaphragms was 18 mm, that between the electrodes 40 mm; the area of the diaphragms was 10 dm^2 , that of the electrodes 8 dm^2 .

Electrodialysis was carried out with current densities of 4, 8, 12, 16 and 24 ma/cm^2 and at temperatures of 20° , 40° and 60°C . In each test a total of 64 amp. hr was passed through, the duration of the experiments therefore varying with the current density and amounting to 16, 8, 5 1/3, 4 and 2 2/3 hours.

The course of the sodium sulphate removal in terms of time, current density and temperature and the course of the acidity of the dialysate are evident from the graphs 2, 3 and 4.

The conclusions of his experiments read as follows:

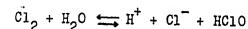
- a. desalting with two identical diaphragms is possible.
- b. the current yield increases by increasing the temperature and reducing the current density; the effect of the temperature is largest when current densities are small.
- c. the increase of the acidity in the middle compartment is minimal at a high temperature and a low current density.

F. The electrode processes.

1. Introduction.

If the cathodic compartment contains raw water during electrodialysis sodium hydroxide and hydrogen will be formed at the cathode. If the anodic compartment contains untreated water the chloride ions discharged at the anode will partly combine into chlorine molecules, resulting in the formation of chlorine gas, which is less soluble in water so that part of it can escape.

Part of the chlorine in (molecular) solution is hydrolysed into hydrogen and chloride ions and into hypochloric acid molecules in accordance with the equation:



In section F 2 the hypochloric acid concentrations in the anolyte are calculated for varying conditions, whilst section F 3 deals with the reactions which may result from the simultaneous presence of chlorine, hypochloric acid and chloride ions in the anolyte.

2. The hypochlorite concentration in the anolyte.

It has been found that during the electrodialysis of liquids containing chloride ions great difficulties arise owing to corrosion of the membranes (31, 34, 36, 38, 53). The cause of this trouble must be attributed most probably to the presence of the hypochloric acid.

In Table IV the hypochloric acid concentrations in the anolyte are calculated for various conditions. The computations are in the following form:

The equilibrium constant for the above equation is represented as follows:

$$K = \frac{[\text{H}^+] [\text{Cl}^-] [\text{HClO}]}{[\text{Cl}_2]}$$

The chlorine in molecular solution is in equilibrium with the chlorine gas which is contained in the gas bubbles of the anolyte.

If the partial pressure (p) of this gas is less than 0.6 atm., then Henry's law holds, and $[Cl_2] = H.p$. Because of the low pressure and concentrations one may use these quantities instead of the activities. The concentration of the hypochloric acid in the anolyte now becomes:

$$[HClO] = \frac{[Cl_2] \cdot K}{[H^+] [Cl^-]} = \frac{H.p.K.}{[H^+] [Cl^-]}$$

If in this equation one substitutes the values of H and K at 15°C as found by Whitney and Vivian (54, 55), viz. 9.35×10^{-3} mol/100 g H₂O per atm. and 2.3×10^{-6} mol/100 g H₂O, it becomes:

$$[HClO] = \frac{p}{[H^+] [Cl^-]} \times 2.15 \times 10^{-8} \text{ (mol/100 g H}_2\text{O).}$$

From this equation as well as from Table IV it follows that the hypochloric acid concentration is reduced by a factor 10:

- by reducing the partial chlorine gas pressure by a factor 10,
- by reducing the pH by 1,
- by increasing the chloride ion concentration by a factor 10.

As it appeared not to be difficult to maintain the partial chlorine pressure in the gas phase outside the cell at 10^{-4} atm., $[HClO]$ was calculated for a chloride ion concentration of 3×10^{-2} n (Dutoh brackish water), $p = 10^{-4}$ atm. and $pH = 2$. In these circumstances the concentration of the hypochloric acid in the rinsing liquid was found to be 0.72×10^{-6} n; for $pH = 7$ it was 0.072 n. It is true that the values found by Whitney and Vivian (54, 55) for the constants K and H, deviate approximately 25 to 100% from those of Jakovkin (56). However, this does not alter the value of $[HClO]$, the hydrolysed fraction.

Hence the concentration of the hypochloric acid in the anolyte may be limited e.g. by raising the concentration of the hydrogen ions and/or of the chloride ions in the anolyte. However, if the anodic membrane used is not fully selective, an excessive concentration of hydrogen ions in the anolyte will have to be avoided owing to the

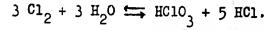
charge efficiency ¹⁾ of the anion to be removed.

3. Reactions between hypochloric acid, chlorine molecules and chloride ions in aqueous solution ²⁾.

The presence of hypochloric acid in the anolyte, formed by the reaction $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, may give rise to various other reactions. However, in the literature there is no agreement on the mechanism of the different reactions of aqueous solutions of chloric and hypochloric acid, whilst the chemical nature of the chlorine-oxygen-compounds is likewise a point of dispute.

It is generally assumed that as a result of the simultaneous presence of chlorine, hydrochloric acid, hypochloric acid, and sodium chloride the following reactions may occur:

- According to Nernst and Sand (57) the following equilibrium is established:



When the chloric acid concentration is calculated with the aid of the equilibrium constant found by Sand (58)

$$K_{200} = \frac{[HClO_3] [HCl]^5}{[Cl_2]^3} = 0.54 \times 10^{-11} \text{ (mol/l)}^3$$

for a partial chlorine pressure of 10^{-5} atm. and for 0.02 n hydrochloric acid, a chloric acid concentration of 1.03×10^{-11} n at 20°C is found ³⁾.

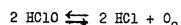
However, much criticism has been levelled at Sand (e.g. (59)). Moreover it is very doubtful whether this equilibrium of Sand still applies to the low concentrations occurring when water is desalinated.

¹⁾ See section V B.

²⁾ the following considerations are taken from a T.N.O. internal report by Dr C.L. de Vries.

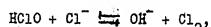
³⁾ $[Cl_2]$ is calculated with the values of K_{200} and H_{200} as found by Whitney and Vivian (54, 55), viz. 2.44×10^{-6} (mol/100 g H₂O) and 7.75×10^{-3} (mol/100 g H₂O per atm.)

b. The decomposition of hypochloric acid according to



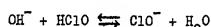
plays a very minor role (60, 61).

c. Hypochloric acid acts upon chlorides in accordance with the equation

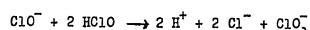


which reaction is strongly dependent on the concentration of the hypochlorite (62).

The hydroxyl ions formed can now react in accordance with

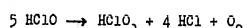


and if the concentration of ClO^- becomes considerable, the reaction



takes place with measurable velocity. On the other hand at low concentrations ClO_3^- is formed slowly.

d. If the hypochloric acid is regarded as one of the intermediate products of the reaction between photo-activated chlorine molecules and water, it may react as an oxygen acceptor and give rise to the formation of chloric acid, perchloric acid and hydrogen peroxide (61)-the formation of oxygen being unimportant (63)- e.g.



However, Allmand and his co-workers deny the formation of perchloric acid (64).

When chlorine water is placed in ultraviolet light, conversion takes place into chloric acid which can also be considered as the end product of the photolysis of chlorine water and hypochloric acid solutions (60) and of solutions of chlorine dioxide in water (65).

Summarizing we may therefore expect that if the concentration of the hypochloric acid in the anolyte can be kept sufficiently low, and the electrodialysis is not carried out in sunlight, practically no other chlorine oxygen compounds will be generated.

IV. ENERGY CONSUMPTION OF ELECTRODIALYSIS.

A. Introduction.

Energy consumption should be kept as low as possible. For this purpose it is necessary to become acquainted with the various factors of which it is composed. Energy losses during electrodialysis exist in heat generation and in formation of by-products, e.g. by formation of hydrogen, chlorine, caustic soda, hypochloric acid.

The energy consumption in the electrodialysis cell is given by the equation:

$$w = \frac{1}{V} \int_{t_0}^{t_k} E \cdot I \cdot dt \text{ Wsec/cm}^3$$

when V is the volume of the dialysate in cm^3 . If E and I are constant this equation becomes: $w = \frac{E \cdot I \cdot t}{V}$.

The terminal voltage E can be regarded as the sum of the electrode-potentials (E_{el}), the voltage drops caused by the Ohmic resistance of liquids (E_i) and the voltage drops across the membranes (E_m).

$$E = E_{el} + E_i + E_m.$$

The factors influencing E_{el} , E_i and E_m will be discussed in the sections IV B, C and D. In section IV E a summary will be given of the factors which might lower the terminal voltage, while in section IV F the quantity of charge passed through ($I \times t$) will be considered.

The determination of the desalting effect q (see section IV F) and of energy consumption for desalting of water, taken from experimental figures, is discussed in section IV G.

B. Electrode potentials¹⁾.

1. Introduction.

The occurrence of a certain potential when an electrode is immersed in a liquid and no passage of current takes place can be taken as a known fact.

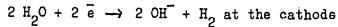
During the passage of current a considerable overvoltage frequently occurs, i.e. a higher voltage must be applied to the electrodes than the theoretical equilibrium potential.

The magnitude of the sum of the electrode potentials (E_{el}) is not a very important factor with a high terminal voltage, but with low terminal voltages such as are applied in desalting water the energy loss caused by this potential may be a substantial percentage of the total energy consumption.

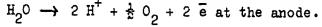
The overvoltage is dependent on the current strength, the composition of the electrolyte, the nature of the electrode surface and on other factors, the influence of many of them not yet being fully known. Although overvoltage has already been studied for some 45 years, there is still much confusion, the results of the various researchers showing large differences.

The following distinctions are made: hydrogen overvoltage, oxygen overvoltage, chlorine overvoltage, concentration and polarisation overvoltage, etc. The expressions cathodic overvoltage or anodic overvoltage are also in use.

The magnitude of the overvoltage is connected with the rate of reactions taking place at the electrodes, viz:



and



¹⁾ For more details on this subject, tables, diagrams, etc. see "Literatuurstudie betreffende het optreden van overspanning, in het bijzonder bij elektroodialyse" by Ir B.C. Lippens, T.A.-report 264 (published by the General Technical Department T.N.O.).

The total voltage drop at the electrodes (E_{el}) is composed of an anodic voltage drop (E_a) and a cathodic one (E_c). Hence:

$$E_{el} = E_a + E_c$$

A low reaction rate causes a high overvoltage, and only in the case of an infinitely high reaction rate the overvoltage is nil.

There are a great many theories and hypotheses about the nature of the reactions which occur at the electrodes upon current passage. The closest study has been made of hydrogen overvoltage. A.o. this is connected with the fact that measurements can be made fairly easily with a reversible hydrogen electrode. In the case of oxygen no such electrode is known and furthermore many difficulties arise owing to the corrosion of the electrode material. Therefore fewer data about oxygen overvoltage are found in literature.

Much work on this subject is done by Tafel (66).

2. The influence of various factors on overvoltage.

a. Current density.

According to Knobel, Caplan and Eiseman (67) in the case of hydrogen overvoltage on increasing the current density there is always a top limit of 1.3 volts, provided there are no secondary reactions.

Azzam and Bockris (68) however, found that at very high current densities the overvoltage often rises considerably, while there is sometimes a kind of hysteresis if the density is first increased and then diminished again. The results are difficult to reproduce, however.

b. Temperature.

Increasing the temperature lowers the overvoltage. At low current densities the influence of the temperature is determined mainly by the temperature coefficients of the diffusion, reaction rate, etc. At high current densities, when the entire electrode is covered with a gas film, the predominant factor is the ease of formation of the gas bubbles; the temperature coefficient of the overvoltage therefore seems to be independent from the electrode material employed.

c. Pressure.

There is no agreement as to the influence of the pressure. Goodwinn and Wilson (69) found that overvoltage decreased with increasing pressure (pressures of 5-100 cm of water). Bockriss and Parsons (70), however, found that -allowing for the influence of the pressure on the equilibrium potential of hydrogen- no change in overvoltage with varying pressure could be established with certainty.

d. Nature of the electrode material.

As there is no agreement as to the way in which overvoltage ought to be or can be determined, it is hardly surprising that literature quotes very varying values for the overvoltage with a given electrode. Differences as high as 1 v may occur between the lowest and highest values stated for overvoltage for an electrode of a certain metal and for the same current density. (see Appendix III of the T.A. Report mentioned before).

Oxygen overvoltage is still less reproducible and here again the observed values do not agree.

Appendix IV of the T.A. Report 264 contains a number of values for oxygen overvoltage in a 1 mol solution of potassium hydroxide. In general metals with a low melting point (Hg, Au, Pb, Zn, Cd) exhibit a high overvoltage and those with a high melting point (Mo, W, Pd) a low overvoltage. Classified according to atomic number the metals display a certain periodicity (see Appendix VI, T.A. Report 264).

e. Finish of the electrode surface.

Research into the overvoltage of hydrogen on metal electrodes with a rough surface (metal-ceramics and powders) by Koezmin (71) (iron), Moertázajew (72) (cobalt) and Maitak (73) (copper) indicates a possibility of reducing this overvoltage by the use of metal powder as cathode material.

A recent investigation (74) has shown that hydrogen overvoltage can be lowered by electrolytically precipitating a film of finely divided metal on a solid cathode. At a current density of

100 ma/cm² in this way a lowering of the overvoltage of 452 mv was obtained with nickel as the cathode material; for the metals platinum, iron, copper, silver, bismuth and tin these values were respectively 552, 405, 221, 406, 100 and 270 mv. According to the authors of the latter investigation it is proved in a number of cases that such reduction is not only the result of surface enlargement through roughening, but mainly of increasing the rate of discharge of the hydrogen ions.

f. Impurities.

Only recently the conclusion has been reached that the presence of very small quantities of impurities in the electrode material has an important influence on overvoltage. Using platinized platinum Bockriss and his co-workers (75, 76) found that 10⁻¹⁰ mol. arsenic per litre caused a considerable increase in overvoltage. The kind of base metal determines the magnitude of the influence of the impurity upon the overvoltage.

g. Time.

According to previous research there is a certain connection between the extent of the overvoltage and the time during which current is passed through. According to Hickling and Salt (77, 78) this fact has only been established experimentally and, at the time of their publications, no theoretical explanation of the phenomenon could be given.

Generally speaking the curve indicating the relation between the extent of overvoltage and the logarithm of the time is a straight line with a certain slope relative to the coordinate axes. The kind of the electrode material, impurities and other factors influence the trend of the curve.

Even after careful purification of the electrode material, the overvoltage was found to rise with time. A certain number of minutes after switching on the electric current, the overvoltage reaches a constant value (30-90 min.). It may be that in this period of time part of the electrode material is dissolved (70, 75, 77 t/m 84).

h. Polarisation.

According to Goodwin and Knobel (79) overvoltage drops if alternating current is superimposed on the direct current. The reduction in overvoltage probably is caused by partial depolarisation of the electrode for the time that the resulting voltage is lower than the decomposition voltage. The extent to which overvoltage is reduced is determined by the ratio of the voltages of both electric currents.

In general the addition of depolarisers reduces the overvoltage. Hickling and Salt (80) found that oxygen bubbled along an electrode considerably reduced hydrogen overvoltage. This, however, depends upon current density: above a specific value there is a sudden increase in overvoltage until it has reached "normal" value. The higher the oxygen concentration, the higher this "critical" current density seems to be (see Graph 5).

Chromates, wolframates, titanates, etc. likewise reduce the overvoltage. These substances stay unaltered (85).

i. Ultrasonic vibrations.

According to Cupr (86) and Piontelli (87) ultrasonic vibrations of about 1200 kc/sec seem to reduce overvoltage.

3. Reduction of overvoltage in electrodialysis.

There are drawbacks to the use of depolarisers in electrodialysis because the ions of the substances under consideration (molybdates, chromates, etc.) will pass through the membrane into the liquid being treated.

As to the use of oxygen on the cathode, very little is known positively. Analogously it can be expected that hydrogen will reduce the anodic (oxygen) overvoltage. This is a mere speculation however; further research will have to show how far this is true.

With regard to the use of ultrasonic vibrations results are still too preliminary to permit a fair judgement of its usefulness.

With regard to the factors mentioned in section IV.B. 2 it can be stated now that in electrodialysis the sum of the electrode potentials may be reduced by selecting an electrode material which involves the

lowest possible overvoltage and/or by roughening the electrode surface as described on page 50.

Frequently (a.o. in desalting water) the electrode material is determined by other factors -e.g. resistivity to corrosion- and therefore in such cases reduction of the overvoltage is only possible by surface roughening.

As in electrodialysis magnetite is an important electrode material a few data are given in Tables VI and VII (88, 89). For further information on overvoltage at magnetite electrodes we refer again to report T.A. 264.

C. Voltage drops caused by Ohmic resistance.

1. Introduction.

The voltage drop caused by the Ohmic resistance in the cell depends on this resistance and the current strength in accordance with Ohm's law:

$$E_i = I \cdot R$$

The resistance in the cell (R) is the sum of the resistances in anodic compartment (R_a) cathodic compartment (R_c) and dialysate compartment (R_d). The following equation applies to each of these resistances:

$$R = \rho \cdot \frac{d}{A} \cdot \frac{1}{\lambda}$$

therefore if all cross sections of the liquid have the same area:

$$E_i = \frac{I}{d} \cdot \sum \delta \rho \cdot d \sum \delta \rho^2$$

The sections IV.C 2 and 3 are devoted to the relation between the voltage drop caused by Ohmic resistance (E_i), the specific conductances (λ) and the current density (d).

¹) δ = depth of the layer of liquid in question.

²) $\sum \delta \rho$ = sum of the products $\delta \rho$ of the anodic, cathodic and dialysate compartments.

2. Specific conductances.

The voltage drop caused by Ohmic resistance in an electrodialysis cell is thus proportional to the sum of the products of the specific resistances of the liquids and the depths of the layers of liquid in each of the compartments. In the rinsing liquids the specific resistance is dependent upon the electrolyte concentration and decreases with increasing concentration. At the same time, however, back-diffusion will increase, i.e., diffusion towards the dialysate compartment. This in turn can be reduced by increasing the rate of refreshing of the electrode rinsing liquids. In order to obtain a minimal energy consumption a definite combination of rinsing liquid composition and refreshing rates must be found for each individual case of electrodialysis.

The depth of the liquid layer in the various compartments depends upon the dimensions of the cell. In the case of very slight depths the pumping power needed to circulate the rinsing liquids at the required rate amounts to considerable values, so that reduction of the depth of the various compartments has a limit below which further decrease does not pay.

There must be no local variation in the depths of the compartments, in other words the distance of the membranes must be sharply fixed. If the membranes bend inwards, the resistance at the place of the shortest distance will be lower than at the sides. The current density will increase locally, in consequence whereof heat development will also increase. This may give rise to all kinds of unpleasant complications (e.g. denaturation of colloids). In case the membranes should touch there will be practically no desalting. When the membranes bend outwards the resistance in the cell will increase. Should it be desired to keep the current strength at a fixed value, a higher terminal voltage will have to be applied, resulting in a higher energy consumption. In this case the greatest passage of current will be found at the edges where the membranes are trapped between the frames or other mounting accessories. If a membrane bends so far that it touches an electrode, the normal circulation of the rinsing liquid is disturbed and there

will be a local increase in acidity or alkalinity. In consequence of this more acid resp. lye will be introduced into the dialysate.

Therefore the supporting of the membranes is very essential in thin compartments.

To prevent an increased resistance of the electrode rinsing liquids and of the dialysate, degassing is wanted. The gases in the rinsing liquids originate from the electrodes and they should be removed as effectively as possible. The gas content of a rinsing liquid will be lowered by increasing the circulation rate, provided the gases are fully eliminated from the rinsing liquid at the degassing vessel.

If possible, foaming must be avoided too. With slightly viscous liquids and liquids containing electrolytes only, few difficulties are encountered in this respect. It is different if the rinsing liquids are polluted, for instance by proteins; in such cases electrodialysis has to be stopped.

3. Current density.

Another important factor determining the value of E_i is the current density. The desalting effect per m^2 area can be accelerated by increasing the current density, which causes the energy consumption to rise however. The amount of energy consumed by the formation of chemicals (e.g. hydrogen, oxygen, chlorine, caustic soda and hydrochloric acid in electrodialysis of salt water) does not increase in the same proportion, and thus the greater part of the energy introduced is released in the form of heat.

These simple considerations can only be applied if the ratios between the quantities of anions and cations passing through the membranes are independent of current density, which with various membranes is actually the case.

However, the great advantage of increasing the current density is the decrease in time, which means a larger desalting capacity per m^2 of membrane area.

D. Voltage drops at the membranes.

With the use of thin membranes the voltage drop at the membranes is usually rather low so that it has no influence on terminal voltage. This is different when by blocking or chemical conversions -for instance by the introduction of certain chemical groups whereby the membrane acquires a certain electric character: cross-linking or otherwise- resistance in the membrane increases. Care should therefore be taken to avoid fouling etc.

E. Summary.

The following factors may reduce terminal voltage in electro-dialysis:

1. low overvoltage (attained by selection of suitable electrode material and/or roughening of the electrode surface).
2. short distances between membranes and electrodes.
3. low current density.
4. high electrolyte concentration of the rinsing liquids.
5. degassing of dialysate and electrode rinsing liquids.
6. prevention of membrane fouling.
7. the use of thin membranes.

F. The quantity of charge passed through in electro-dialytic desalting.

For electrodialytic desalting the most important item is of course the energy consumption per gramme of the salt to be removed. Beside the factors which lead to minimum terminal voltage (see section IV.B), there will also be several factors which influence the product $I \times t$.

The migration of other ions, the rediffusion of ions already removed and the water transport through the membrane are a.o. the causes that, during desalting of water in a three-compartment cell, all the charge passed through the dialysate is not carried over by chloride ions moving towards the anode and sodium ions moving towards the cathode. Therefore efforts have to be made to ensure that in passing a certain number of coulombs through the dialysate, this liquid is desalted to a maximum degree.

In general our experimental coworkers qualify the desalting effect in various electrodialytical experiments by q , i.e. the number of grammes of salt removed from a compartment per 100 ampère-hours. Therefore in the water desalting investigations q becomes the number of grammes of sodium chloride removed from a compartment per 100 ampère-hours.

The value of q of the salt to be removed electrodialytically from the middle compartment is determined mainly by the values of the charge efficiencies of the cations and anions of the salt for the anodic and cathodic membranes¹). Under certain conditions a high q -value will be obtainable with the use of an anodic or cathodic membrane which at these conditions exhibits a high charge efficiency for the anion or the cation to be removed.

In chapter V it is attempted to deduce theoretically the factors influencing these charge efficiencies. The determination of q from experimental data on the desalting of water will be discussed first.

G. Calculation of energy consumption and desalting effect for the electrodialytic desalting of water from experimental data.

1. Definitions.

In order to be able to express the results of water desalting experiments in terms which can be compared, it is necessary to calculate:

N_E = the number of kWh needed for desalting 1 m³ water over a desalting range of 28 to 8 meq. Cl⁻/l.

q = the number of grammes of sodium chloride removed per 100 amp.-hr in desalting over the same range.

At the same time the following symbols are introduced:

$W(c_p, c_k)$ = the energy consumption in kWh/m³ of a certain experiment for a desalting range from c_p to c_k meq. Cl⁻/l.

$q(c_p, c_k)$ = the number of grammes of sodium chloride removed per 100 amp.-hr in desalting from c_p to c_k meq. Cl⁻/l.

¹) cf. section V.B for the description of these efficiencies.

If $c_p < 28$ and $c_k > 8$ meq. Cl^-/l , then in the same experiment $W(c_p, c_k)$ will be smaller than N_p . As however q represents an average value e.g. q (27, 20) can under certain conditions be higher than q . This might be the case for q if at the beginning of desalting the salt concentrations of the water in the dialysate, anodic and cathodic compartments are the same: as desalting of the middle compartment progresses the counteraction of the diffusion will be greater.

2. Calculation of N_p and $W(c_p, c_k)$.

In every desalting experiment it is possible to measure at the times T_0, T_1, \dots, T_n in hours, the voltages E_0, E_1, \dots, E_n , in volts, the current strengths I_0, I_1, \dots, I_n in amperes and the chloride ion concentrations c_0, c_1, \dots, c_n in meq/l. The energy consumption for the entire experiment in kWh/m^3 is thus:

$$W(c_0, c_n) = \frac{10^{-3}}{V} \int_{T_0}^{T_n} E(T) \cdot I(T) \cdot dT$$

with V representing the volume of the dialysate (in m^3) and the index n the number of time intervals.

For any other given concentration range $c_p - c_k$ meq Cl^-/l , $W(c_p, c_k)$ can be calculated from the integral:

$$W(c_p, c_k) = \frac{10^{-3}}{V} \int_{T_0}^{T_k} E(T) \cdot I(T) \cdot dT \quad (1 \leq k \leq n).$$

Therefore on the basis of experimental data it is desired to obtain as simply as possible the most (then) accurate value practicable for the above integrals, i.e. for the integral:

$$\int_{T_0}^{T_n} f(T) \cdot dT,$$

the functional relation $f(T)$ not being known.

If $f(T)$ is determined, i.e. if E and I are measured at sufficient close (equal) intervals linear interpolation is the proper way and $f(T)$ is adequately approximated by this broken line.

When the above mentioned condition is fulfilled the above integral can simply be found from the experimental data.

3. Calculation of q and $q(c_p, c_k)$.

In a three-compartment cell the number of grammes of sodium-chloride removed from the dialysate per 100 amp.hr., $q(c_p, c_k)$, is equal to the total number of gram equivalents chloride removed, multiplied by the quotients $58.5/35.5$ and $100/I \times T$. The total number of gram-equivalents Cl^- removed is equal to the difference between $10^{-3}(V \cdot c_p)^d$ and $10^{-3}(V \cdot c_k)^d$ if the volume of the dialysate V^d is expressed in litres, and therefore holds

$$q(c_p, c_k) = 10^{-3} \cdot \frac{(V \cdot c_p)^d - (V \cdot c_k)^d}{IT} \cdot \frac{58.5}{35.5} \cdot 100 = 0.165 \frac{(V \cdot c_p)^d - (V \cdot c_k)^d}{IT}$$

$$\text{and } q = 0.165 \frac{28 V^d - 8 V_k^d}{IT}$$

In a two-compartment cell the elimination of chloride ions takes place in the anolyte, and in that case V^d and c^d in these equations become the volume (in litres) and concentration (meq. Cl^-/l) of the anolyte, viz. V^a and c^a .

Removal of the chloride ions takes place at the anode, where conversion into chlorine and hypochloric acid takes place. The chlorine partly escapes as gas and can be determined experimentally.

$[\text{Cl}_2]$ henceforth means the number of milli equivalents of chlorine gas determined.

The remainder of the chlorine remains in solution and can be quantitatively determined there together with the various chlorine-oxygen compounds.

$[\text{act.Cl}]$ henceforth means the number of milli equivalents of "active chlorine" in the anolyte (and possibly due to diffusion in the dialysate as well), i.e. dissolved chlorine gas and the other chlorine-oxygen compounds together.

It will now be clear that in a three-compartment cell:

$$[(V.c)_p - (V.c)_k]^a = [Cl_2] + [act.Cl] + [(V.c)_k - (V.c)_p]^a + [(V.c)_p - (V.c)_k]^c$$

and in a two-compartment cell:

$$[(V.c)_p - (V.c)_k]^a = [Cl_2] + [act.Cl] + [(V.c)_k - (V.c)_p]^c$$

so that $q(c_p, c_k)$ can be determined as well directly as indirectly in a three- and a two-compartment cell.

4. The error in $N_p \cdot W(c_p, c_k)$, $q(c_p, c_k)$ and $q(c_p, c_k)$ caused by measuring chloride ion concentrations.

The inaccuracy in determining the chloride ion concentrations c_p and c_k leads to an error in $W(c_p, c_k)$ and $q(c_p, c_k)$. The value of this error will be relatively higher as the accuracy in measurement and the difference $(c_p - c_k)$ are less. The influence of the experimental error in the determination of the chloride concentrations c_p and c_k will be clear from the following examples in which an experimental error of 0.3% has been assumed.

$$\begin{aligned} c_p &= 28 \pm 0.3\% = 28 \pm 0.084 \\ c_k &= 8 \pm 0.3\% = 8 \pm 0.024 \\ c_p - c_k &= 1 \pm 0.165 = 1 \pm 16.5\% \end{aligned}$$

and

$$\begin{aligned} c_p &= 9 \pm 0.3\% = 9 \pm 0.027 \\ c_k &= 8 \pm 0.3\% = 8 \pm 0.024 \\ c_p - c_k &= 1 \pm 0.051 = 1 \pm 5.1\% \end{aligned}$$

If $c_p = 28/c_k = 8$ meq. Cl^-/l , the degree of accuracy is 0.54%, as shown by the calculation below.

$$\begin{aligned} c_p &= 28 \pm 0.3\% = 28 \pm 0.084 \\ c_k &= 8 \pm 0.3\% = 8 \pm 0.024 \\ c_p - c_k &= 20 \pm 0.108 = 20 \pm 0.54\% \end{aligned}$$

In the same way the values in the following table are calculated for various accuracies in measurement and differences in concentration. This is also the error in $W(c_p, c_k)$, $q(c_p, c_k)$ and $q(c_p, c_k)$ ¹.

Error in $(c_p - c_k)$ (per cent) in the case of various values of c_p and c_k

$c_p - c_k$ (mg Cl^-/l)	c_p (mg Cl^-/l)	Accuracy titration (per cent)			
		0.6	0.3	0.2	0.05
700	1000	1.1	0.6	0.4	0.1
100	1000	11.4	5.6	3.8	0.9
	400	4.2	2.1	1.4	0.4
35.5	1000	33.2	16.6	11.1	2.8
	335.5	11.1	5.6	3.7	0.9

These errors are caused by the actually measured concentrations c_p and c_k . In order to obtain anything like reliable results the measuring points (t_k, c_k) can only be used if the accuracy in measurement of c_k is 0.05% and the points are no closer together than 35.5 mg. In that case about eighteen or nineteen points are obtained in the range from 1000 to 300 mg Cl^-/l . In all other cases the best thing is to plot "as well as possible" (i.e. in the sense of the method of the smallest squares) a smooth curve along the measured points $C(t)$ and use the concentrations c_p and c_k determined from this curve for further calculations.

If it is desired therefore in certain cases to determine $W(c_p, c_k)$ and $q(c_p, c_k)$, this can only be done with any degree of

¹) See section V.E

accuracy if the range (c_p, c_k) is not taken too small. The limit for this depends upon the accuracy of determining the chloride ion concentrations.

The error in the "indirectly" measured q's depends chiefly on the accuracy of determining the chlorine and active chlorine concentrations.

V. CHARGE EFFICIENCY.

A. Introduction.

A membrane is placed between two solutions containing various cations and anions in different concentrations and with different mobilities. On either side of the membrane an electrode is placed, after which current is passed through the solution. Now what is the charge efficiency for each of these ions under the influence of the electric field, the water transport through the membrane and the diffusion together?

In section V.C a general equation is found for the current density efficiency of these ions, followed in section V.D by a simpler computation, made on the basis of a very simple conception of the membrane.

Since, in the material dealt with in section V.C. and V.D., the terms current density efficiency, charge efficiency and current efficiency will be used these concepts are first described in detail in section V.B.

In section V.E we describe the way in which the charge efficiency of the chloride ion for the cathodic and the anodic membrane is calculated from the experimental data relating to electro(dia)lytic desalting of water.

Finally, in section V.F a number of charge efficiencies are given which were found by Zhukov (52) and Billiter (29) in their experimental investigations of electrodialysis.

B. Definitions of the various efficiencies.

The following efficiencies are each defined in respect of the R^- -ions in solution, possibly together with other ions. It should be born in mind however, that the definitions can be applied for any ion.

1. Current density efficiency.

Current density efficiency \rightarrow the direction x is understood to be the fraction of the total current carried by the R^- -ions through an infinitesimal surface element \rightarrow situated at

a random point (P) of the electrolyte (the orientation of \vec{df} is given by the unit vector \vec{x} : $\vec{df} = df \cdot \vec{x}$)

$$\eta_R^i(P; \vec{x}) = \frac{\vec{i}_R \cdot \vec{df}}{\vec{i} \cdot \vec{df}} = \frac{\vec{i}_{Rx} \cdot \vec{x}}{\vec{i} \cdot \vec{x}} = \frac{i_{Rx}(P)}{i_x(P)} \quad 1)$$

In stating current density efficiency therefore it is always necessary to give the orientation of the unit area considered in the point concerned.

Reference is sometimes made to "the" current density efficiency in a point P of the electrolyte which then means the current density efficiency in the direction \vec{i} (the orientation of the unit area at that point coincides with the total current density vector: $\vec{x} = \vec{i}/i$).

$$\eta_R^i(P) = \frac{\vec{i}_R \cdot \vec{i}}{i^2}$$

2. Current efficiency.

The current efficiency for an arbitrary surface (S) situated entirely in the electrolyte is that part of the total current (I) through the surface, which is carried by the R^- -ions.

$$\eta_R^I(S) = \frac{I_R(S)}{I(S)} = \frac{\int \vec{i}_R \cdot \vec{df}}{\int \vec{i} \cdot \vec{df}}$$

In the stationary state $\eta_R^I(S) = \eta_R^I(S')$ if S and S' form a closed surface.

The current efficiency in respect of the R^- -ions of a membrane is that part of the total current through the membrane which is transported by the R^- -ions.

$$\eta_{M,R}^I = \frac{I_R}{I}$$

¹⁾ (i_{Rx} and i_n are the normal components of i_R and i)

3. Charge efficiency and coulomb efficiency.

The charge efficiency for an arbitrary surface (S) situated entirely in the electrolyte solution is that part of the total charge Q flowing during a time interval t through that surface, which is transported by the R^- -ions. This efficiency is sometimes also called (disputable!) the coulomb efficiency.

$$\varphi_R(S) = \frac{Q_R(S)}{Q(S)}$$

The charge (coulomb) efficiency so defined is therefore a kind of average efficiency for the time interval (0, t). The charge efficiency of the R^- -ions at a given moment t then is:

$$\varphi_R(S; t) = \frac{dQ_R(S; t)}{dQ(S; t)} = \frac{I_R(S; t) \cdot dt}{I(S; t) \cdot dt}$$

In the stationary state this fraction is independent of time, and the charge efficiency therefore becomes a constant, viz:

$$\frac{I_R(S; t)}{I(S; t)} = \eta_R^I(S)$$

It is only in the stationary state therefore that for a random surface S situated entirely in the electrolyte the current efficiencies and charge efficiencies are numerically the same.

The charge (coulomb) efficiency of the R^- -ions for a membrane, for a specific process, during the time interval (0, t), in respect of the R^- -ions means: that part of the charge which has flowed through the membrane in the time interval t, which is carried over by the R^- -ions. This therefore is again an average efficiency. It is only in the stationary state that this efficiency becomes a constant

$$\varphi_{M,R} = \frac{Q_R}{Q}$$

while at the same time $\varphi_{M,R}$ becomes equal to $\eta_{M,R}$.

It follows from the above definitions that in the stationary state in a homogeneous field current density efficiencies, current efficiencies and charge efficiencies are numerically equal, and that in such case the following computations of the current density efficiencies for the various ions can also be used for calculating the charge efficiencies.

C. Derivation of a general expression for current density of an ion in a system of a number of ions in the case of charged membranes.

1. General equation for current density of an ion.

Teorell (90) finds an expression for the current density of the anions and cations under the conditions mentioned in section V.A. making the following assumptions:

- all cations and anions are monovalent.
- the water transport through the membrane is negligible.
- distribution of the so-called "fixed charges"¹) is the same over the entire pore and over the entire membrane.
- Planck's method (92), developed for treating the electrolyte diffusion is correct, i.e. there is no linear mixing of the ions in the membrane as assumed by Henderson (93).
- the state is stationary.

Teorell (92, 94) uses the fundamental equation of the "ionic flux" i.e. the number of coulombs transferred per sec. by a certain ion species M at an arbitrary place within the membrane through a unit area perpendicular to the direction of diffusion (= current density of that ion in the membrane pores = i_M). Hence for a monovalent cation is

$$i^+ = -u' \cdot a' \left(\underbrace{\frac{RT}{a} \cdot \frac{da'}{dx}}_{\text{osmotic term}} \pm \underbrace{F \cdot \frac{dq}{dx}}_{\text{electric term}} \right)^2$$

¹) See e.g. (91).

²) The concentrations in the membrane are here indicated by a's, in the free solution by c's.

After introducing Planck's variable ζ (see note 2, Table VIII and page 69) for $e^{(F/RT)}_E$ equations are obtained for the current densities of each monovalent cation and anion which, for the stationary state after integration from $x = 0$ to $x = \delta$ give the general equation of Teorell:

$$i^+ = -u' \cdot K^+ (a^+ \zeta - a^+)^{-1}$$

According to Teorell it appears from this equation that if a membrane is placed between two solutions with different monovalent ions and if current passes through the current density of each ion is proportional to its mobility in the membrane and to the difference of its electrochemical activities at the membrane surfaces².

All cations have the same proportionality constant, while this is likewise the case with the proportionality constant for the anions. In general the proportionality constants of cations and anions, each a product of three terms, will not be equal and will have different values for different membranes. Their denominator includes the thickness of the membrane.

This equation of Teorell's is generally applicable as it applies both to current free systems (free diffusion : $I = 0$) and to systems where current passes through ($I \neq 0$). Numerical evaluation of this general equation in a specific case has to be performed in different stages (cf. pag. 469 of the article in question).

In Table VIII also several less general equations are recorded.

Graph 6 is a completely worked out example at passage of current and equal total concentrations ($c_1 = c_2$). Between solution 1 (90 HCl + 10 NaBr³) and solution 2 (10 HCl + 90 NaBr³) a membrane ($\omega \bar{x} = 200$)³ is placed: the Donnan potentials at the membrane surfaces π_1 , and π_2 are + 22 mv and - 22 mv resp. The current densities of the ions

¹) This equation is given in full detail in Table VII. Abridged computations are given in Appendix 6.

²) These activities are $a_+ \zeta$ and a_- respectively as the value of ζ varies from 0 to ζ through the membrane.

³) Arbitrary concentration units.

and the total current density are plotted as a function of various applied potentials : the potential difference equals the sum of these Donnan potentials and the diffusion potential in the membrane.

2. Correction factor for water transport through the membrane.

Water transport through the membrane is not always negligible and strictly speaking the equation is not yet general enough. If one assumes a constant flow of liquid perpendicular to the membrane with a rate of μ cm/sec, the equation: $i^+ = -u'$. A' (cf. Appendix 6), becomes:

$$i^+ = (-u' A' - \mu c^+) \text{ and}$$

$$i^+ = R T' \cdot u' \cdot a^+ \left[\frac{d(\ln a^+ \zeta)}{dx} + \frac{\mu}{RTu'} \right]$$

So far, however, attempts to obtain a general solution for this equation have been unsuccessful in respect of charged membranes.

3. The ratio influx/outflux for each ion.

The current density of each ion can be represented by

$$i^+ = -f^+ \cdot u' \cdot (a_2^+ \zeta - a_1^+)$$

in which f^+ is a proportionality constant. It appears to be composed of an influx

$$-f^+ \cdot u' a_2^+ \cdot \zeta$$

in the direction $2 \rightarrow 1$ and an outflux

$$+f^+ \cdot u' a_1^+$$

in the direction $1 \rightarrow 2$.

The ratio influx for a cation is therefore

$$\frac{a_2^+ \zeta}{a_1^+} = \frac{c_2^+ r_2 \zeta}{c_1^+ r_1}$$

r represents the constant Donnan ratio:

$$r = \frac{a_2^+}{c_2^+} = \frac{c_1^-}{a_1^-}$$

The expression for the ratio influx outflux is particularly appropriate for radio active tracer experiments.

If the resulting current approaches zero it is possible to speak of an individual ion distribution equilibrium, in which influx = outflux. In this case we find

$$\left(\frac{a_2^+}{a_1^+} \right) = \zeta$$

It appears from this equation that ζ has also the meaning of the ratio of equilibrium concentrations.

4. Ratio between current densities of two cations and of two anions.

As i^+ has the same value for both ions the ratio between the current densities of two cations becomes:

$$\frac{i^+}{i^+} = \frac{u'}{u''} \cdot \frac{a_2^+ \zeta - a_1^+}{a_2'' \zeta - a_1''}$$

In the same way

$$\frac{i^-}{i^-} = \frac{v'}{v''} \cdot \frac{a_2^- - a_1^- \zeta}{a_2'' - a_1'' \zeta}$$

Hence it appears that the ratio of the current densities of two cations in the same system and under the conditions mentioned on page 66 is independent of the charge of the membrane and the thickness of the membrane. It is proportional to the ratio of the mobilities within the membrane and to the ratio between the differences of their electrochemical activities at the membrane surfaces.

5. The current density efficiency of each ion.

The current density efficiency η^+ of each ion is obtained by dividing the second term of the general equation by the total current density in the pores

$$\eta^+ = \frac{i^+}{i}$$

In this equation $i = \sum i^+ - \sum i^-$.

Hence in η^+ the denominator consists of a sum of terms, each of which is proportional to the mobility of an ion in the membrane and to the difference of its electrochemical activities at the membrane surfaces, and inversely proportional to the thickness of the membrane. In addition the numerator also consists of such a term.

D. A simple calculation of the current density efficiency of an ion present in a system of a number of ions in the case of non-selective membranes.

1. General remarks.

To make calculations as simple as possible various basic assumptions -partly incorrect- are made. The assumptions a, b and c of Teorell (page 66) are adopted also in this case. In addition the following assumptions are made:

- Fixed membrane charges are either absent, or their influence is completely negligible.
- The external electric field in a membrane pore is homogeneous and longitudinal to the pore.
- All the quantities concerned are variable only longitudinal to the pore.

The current density of a cation in membrane pore is represented by

$$i^+ = u' \cdot \gamma^+ \cdot \frac{dE}{dx} - D^+ \cdot \frac{d\gamma^+}{dx}$$

in which $D^+ = \frac{R T}{F} \cdot u'$

Similar equations can be derived for the other cations and anions. By adding these equations and by bearing in mind that

$$i = \sum i^+ - \sum i^-$$

$\frac{dE}{dx}$, the real field strength at each point, can be computed. After substituting $\frac{dE}{dx}$ in the equation mentioned above and then dividing by i we obtain a differential equation for the current density efficiency of the cation in question. After integration of this differential equation, introduction of the boundary conditions $c^+(0) = c_1$ and $c^+(\delta) = c_2$, a direct relationship can be established between current density efficiency, concentrations, membrane thickness and current density.

These integrations have been effected for a two- and a three-ion-system, detailed calculations for which are given in Appendix 7.

2. The two-ion-system.

The current density efficiency of e.g. the cation in a two-ion-system is given by the equation:

$$\eta_+^i = n^+ + \frac{D^*}{i \delta} (\gamma_2 - \gamma_1)$$

in which D^* represents the "mixed diffusion" coefficient of the salt:

$$D^* = \frac{2 D^- D^+}{D^- + D^+}$$

γ_2 and γ_1 are the concentrations on either side of the membrane (coulombs per cm^3).

It appears from this result that the current density efficiency is obtained by increasing (or decreasing) the electrical transference number by a diffusion term. The latter increases in importance as the difference in concentration ($\gamma_2 - \gamma_1$) is greater and the thickness of the membrane is less (see Graph 7). If $\gamma_2 = \gamma_1$ the diffusion effect is eliminated and the current density efficiency equals the electrical transference number.

Numerical evaluation of this equation involves the substitution

of the actual current density in the membrane pores (i) by the current density as calculated per cm^2 membrane area (d). These two quantities are connected by the "effective membrane area" (O_e), which is that part of the membrane which corresponds with the openings of the pores.

The interrelation is

$$i = \frac{d}{O_e}$$

According to experimental data on cellophane membranes, made by the firm Kalle and Co. (quality OJ; calibre 70) the value $O_e = 0.12$ has been adopted. The thickness of this sample was $\delta = 0.015 \text{ cm}$.

Taking into account the factors, necessary for conversion of chemical concentration values into the proper units and substituting the numerical values for n^+ and D^{\ddagger} we obtain in the case of HCl:

$$\eta_{Cl^-}^i = 0.179 + 22.8 \frac{c_2 - c_1}{d}$$

(c_2 and c_1 in $\text{eq.}/\text{l}$, d in ma/cm^2).

This equation is represented diagrammatically in Graph 8, where the current density efficiency is plotted as a function of the concentration difference for various current densities.

It appears that when $c_1 = c_2$ the current density efficiency amounts to 18 per cent.

In the region $c_1 - c_2 > 0$, diffusion brings about a decrease in the current density efficiency which is greater as d is smaller, in the region $c_1 - c_2 < 0$ there is a corresponding increase. For an infinitely great current density diffusion relatively plays no further part and the slope of the curve therefore approaches zero. If the thickness of the membrane for a given current density is made f times as great, this has the same effect as if the current density were taken f times as great with the same thickness. In this way the array of curves of Graph 8 can also be regarded as curves for various membrane thickness at a constant current density.

3. The three-ion-system.

We have in mind a mixture of a salt (MR) with an acid (HR), as for

instance in the anodic membrane of an electrodialysis cell. Section II of Appendix 7 contains the derivation of an expression for η_R^i , the current density efficiency of the common R^- -ion. The result was:

$$\frac{\chi_2(\eta_R^i \cdot z + 2) - v \gamma_2^-(z + 2)}{\chi_1(\eta_R^i \cdot z + 2) - v \gamma_1^-(z + 2)} = \left(\frac{\gamma_2^-}{\gamma_1^-} \right) \left(\frac{\eta_R^i \cdot z + 1}{\eta_R^i \cdot z + 2} \right)$$

$$\text{in which } Z = \frac{i \cdot \delta}{(\gamma_2^- - \gamma_1^-) \cdot D^-}$$

This is an implicit exponential function of the current density efficiency η_R^i . With the aid of this equation it is now possible numerically to show diagrammatically the dependence of the current density efficiency upon each other quantity.

Several general remarks follow from this derivation. It appeared for instance, that

$$\frac{d^2 \gamma^-}{d x^2} = 0, \text{ therefore } \frac{d \gamma^-}{d x} = \frac{\gamma_2^- - \gamma_1^-}{\delta}$$

It is interesting to note that the latter conclusion with regard to the R^- -ions applies generally to the total concentration, and therefore to a system with n ions as well. The total concentration has therefore always a linear trend through the pores. On the other hand the trend of concentration of individual ions throughout the pores is definitely not linear (as for instance in Graph 9). Furthermore obviously i and δ are found to be absolute equivalents, viz. as product $i \cdot \delta$. This was also the case in the result of the two-ion-system and continues to apply therefore to a three-ion-system.

Section III of Appendix 7 contains the calculation of the current density efficiency of an ion in a two-ion-system from that in a three-ion-system.

4. Conclusions from calculations.

The principal conclusions arrived at from the simple calculations made in the three preceding paragraphs are:

- Both in two- and three-ion-systems increasing the current density has the same effect on the current density efficiency of an ion as increasing the thickness of the membrane.
- If diffusion and electrodialysis co-operate it is advisable to have the thinnest possible membrane and the lowest possible current density in order to obtain the maximum current density efficiency. If they counteract, such as for instance happens in the desalting of water, a thick membrane and a high current density are advisable.
- In a system of three ions, A^+ , B^+ and R^- the trend of the concentration of R^- -ions through the pores is linear.

However, this all applies only to a very simple conceptions of membranes !

E. Calculation of the charge efficiency of the chloride ion in the cathodic and the anodic membranes from experimental data of electro(dia)lytic desalting experiments of water.

In the case of electrodialytic desalting of water in a three-compartment cell q is at a maximum if the charge efficiency of the chloride ion in the anodic membrane and of the sodium ion in the cathodic membrane is at a maximum. As a membrane with a high charge efficiency for cations will have a low charge efficiency for anions, it is sufficient to consider only the charge efficiency of the chloride ion in the cathodic membrane and in the anodic membrane, which should then be at a minimum or at a maximum respectively.

When in a certain experiment the dialysate is desalting from c_p^0 to c_k^0 (meq. Cl^-/l), the energy consumption $W(c_p^0, c_k^0)$, and the desalting effect $q(c_p^0, c_k^0)$ are calculated according to the equations in section IV.G. If the concentration and the volume of the catholyte alters during this test from c_p^0 and V_p^0 to c_k^0 and V_k^0 and the concentration and the volume of the dialysate at the same time changes from

c_p^d and V_p^d to c_k^d and V_k^d the number (N) of chloride ions which have passed through the cathodic membrane is:

$$N = (V \cdot c)_p^0 - (V \cdot c)_k^0 \text{ (meq)}$$

The quantity which has passed through the anodic membrane is equal to this difference, increased by the term $(V \cdot c)_p^d - (V \cdot c)_k^d$, i.e.

$$N = \left[(V \cdot c)_p^0 + (V \cdot c)_p^d \right] - \left[(V \cdot c)_k^0 + (V \cdot c)_k^d \right] \text{ (meq } Cl^- \text{)}$$

This latter can also be calculated directly (Cf. page 59) and then amounts to:

$$N = [Cl_2] + [\text{act. } Cl] - \left\{ (V \cdot c)_p^0 - (V \cdot c)_k^0 \right\} \text{ (meq } Cl^- \text{)}$$

The number of coulombs transported by these chloride ions, is obtained by multiplying the value of N with $\frac{96500}{1000}$. The total charge which has passed through the membrane equals $I \times T \times 3600$. Therefore the average charge efficiencies (Cf. page 60) of the chloride ions in the cathodic and anodic membranes during the above mentioned experiments are obtained by multiplying the values of N with the factor $\frac{96500/1000}{I \times T \times 3600} = \frac{2.68}{100 I \cdot T}$.

In this report they are indicated by $\varphi_{cm}(c_p^0, c_k^0)$ and $\varphi_{am}(c_p^0, c_k^0)$ (direct or indirect), in contrast to the charge efficiencies φ_{cm} and φ_{am} (direct or indirect), which relate to the desalting from 28 to 8 meq. Cl^-/l .

To sum up therefore:

$$\varphi_{cm}(c_p^0, c_k^0) = \frac{2.68}{I \cdot T} \left[(V \cdot c)_p^0 - (V \cdot c)_k^0 \right] \text{ } 10^{-2} \dots \dots \dots (1)$$

$$\varphi_{am}(c_p^0, c_k^0) \text{ (indirect)} =$$

$$= \frac{2.68}{I \cdot T} \left\{ \left[(V \cdot c)_p^0 + (V \cdot c)_p^d \right] - \left[(V \cdot c)_k^0 + (V \cdot c)_k^d \right] \right\} \text{ } 10^{-2}$$

$$\varphi_{am}(c_p, c_k) \text{ (direct)} = \frac{2.68}{I \cdot T} \left[[Cl_2] + [\text{act.} Cl] - \left[(V \cdot c)_p - V \cdot c)_k \right]^a \right] \cdot 10^{-2} \quad \dots \dots (2)$$

$$\varphi_{cm}(28,8) = \varphi_{cm} \text{ and } \varphi_{am}(28,8) = \varphi_{am}$$

As these charge efficiencies are averages, it is not impossible that in some cases for instance $\varphi_{am}(c_p, c_k)$ will be greater than φ_{am} .

When a two-compartment cell is used, φ_m will mean the (average) charge efficiency of the chloride ion in the membrane, when desalting of the anolyte from 1000 to 300 mg Cl^- /l is considered; if the range from c_p to c_k is being considered, the membrane efficiency will be indicated by $\varphi_m(c_p, c_k)$. It then appears from the above definitions that

$$\varphi_m(c_p, c_k) = \text{equation (1)} = \text{equation (2)}.$$

The errors in the various φ 's and $\varphi(c_p, c_k)$'s caused by the determination of the chloride ion concentrations are given in the table on page 61.

F. Charge efficiencies and current efficiencies found in literature.

Zhukov (52) and Billiter (29) who both studied the electrodialysis process very thoroughly, including the removal of salts from water, calculated several "current efficiencies", R's, from the equation:

$$R = \frac{P}{6796500} \times 100 \quad ^1)$$

Aten (31) also calculated his theoretical "current efficiencies" in this way (Cf. section III.D).

¹⁾ R = the so-called "current efficiency" of an ion or of a salt.

P = the number of gramme equivalents (of the ion or salt concerned) removed from the dialysate.

C = the number of coulombs passed through the dialysate.

The "current efficiencies" found by these investigators, however, are by no means the same as the current- or charge efficiencies defined by us (Cf. section V.B). These efficiencies always relate to an area and therefore the description used by them for an efficiency related to a volume is rather misleading. Their "current efficiencies" far more resemble the q introduced in this report (cf. section IV.G); the number of grammes of salt removed from the dialysate per hundred amp.hr. If their experimental determined P's represent the number of gramme equivalents of salt removed from the dialysate it is possible to calculate q from their "current efficiencies"

$$q = \frac{P \times M}{C} \times 3600 \times 100 \text{ and } R = \frac{P}{6796500} \times 100,$$

$$\text{so} \quad q = M \cdot R \times 0.037 \text{ (g salt/100 amp.hr)} \quad ^1)$$

In the electrodialysis apparatus in which Zhukov studied purification of the water of the Neva (52), the "current efficiency" of the electrodialysis was detected gravimetrically on a 0.01 n solution of calcium sulphate. With a catholyte alkalinity of 0.005 n, the "current efficiency" of the calcium ion increased with decreasing acidity of the anolyte, reaching 36% at 0.001 n. For the sulphate ions a value of 28-29% was attained. This lower value for the anion was to be expected as Zhukov used a pair of negative membranes, viz. two tubular membranes of ceramic material. Nevertheless the observed value is still well above 20%.

Billiter (29) stated that for his equipment (a ceramic anodic and an asbestos cathodic membrane) the "current efficiency" of the salts to be removed was, at its best, 20% but normally did not exceed 12 to 15%. As average molecular weight of these salts he assumed 50.

Stenler and Sirak (96) investigated in electrodialysis a series of membranes to find their "current efficiency" in a 4 n solution of sodium sulphate. For negatively charged pairs of membranes, such as asbestos-ceramic, they state 10 to 18%, for bakelite-gelatine membranes-acetylcellulose 23%.

The pair of negatively charged ceramic membranes selected by Zhukov,

¹⁾ M = molecular weight.

as compared with membranes not electrochemically active, therefore give a higher "current efficiency".

The conclusion of our research in literature is, that although some quantities have been found to which the name "current efficiencies" was given, the literature contains no data on efficiencies as defined by us in section V.B. Nor could we calculate these with the assistance of factual material found in the literature on the subject, as the data required were not complete.

VI. THE EXPERIMENTAL RESEARCH INTO WATER DESALTING.

The experimental research may be divided into five sections, viz.:

- A. Construction of the apparatus.
- B. Investigation of the possibility of desalting with the use of non- or only slightly selective membranes and acid and alkaline rinsing liquids, followed by research into the causes of corrosion of the anodic membrane and the possibility of preventing this.
- C. Desalting research with the aid of selective membranes.
- D. Research into chlorine removal at the anode.
- E. Investigations of the possibility of desalting water by means of reversible electrodes.

These sections will be dealt with one by one. The apparatus used in section VI.E will be described together with the corresponding research (pg.94). Finally this chapter will be concluded with a review of the results of these experiments and the possibilities of water desalting on an industrial scale.

A. Description of the apparatus.

1. Arrangement of the cell.

In the experimental work described in the sections VI.B and VI.C a rectangular electrodialysis cell was used (20 x 40 cm) consisting of an anode (1) of magnetite (thickness 10 mm) and a nickel cathode (2) (thickness 5 mm).

Proceeding in the direction of the cathode (according to the diagrammatic cross-section in Figure 4a) we find between the anode and the cathode resp.:
a rubber sheet (3), cut out as shown in Figure 4b, forming the anodic rinsing compartment,
the anodic membrane (4) with a working area of about 580 cm²,
the dialysate cell (5) in the form of a rubber sheet cut out as shown in Figure 4c,
the cathodic membrane (6): working area approximately 580 cm²,
a rubber sheet (7), cut out in accordance with Figure 4d, and forming the cathodic rinsing compartment.

In the case of non-rigid membranes, such as cellophane membranes, supports in the form of saran or nylon gauze are fitted against that side of the membrane which faces the electrode in order to maintain the thickness of the three compartments at constant values all over the membrane area. By arranging for a slightly higher pressure in the middle compartment than in the outer compartments, the membranes are pressed against the taut supports.

The whole is compressed and sealed by two pressure plates (8 and 9), attached to the outsides of the electrodes. For the desalting experiments in the two-compartment cell with non-reversible electrodes (section VI.B) the same cell was used though the dialysate cell (5) and one membrane (4 or 6) were omitted, so that a cathodic and an anodic compartment remained, separated by a membrane. For the membranes cellophane was used, treated or untreated, supplied by the Visking Corporation, Chicago (thickness dry: 0.12 mm, wet: 0.22 mm).

2. Circulation of the liquids.

The anodic rinsing liquid is fed through hole 10 to the bottom of the anodic compartment, which it leaves again via hole 11.

The cathodic rinsing liquid is transported via holes 12 and 13, whilst the dialysate is fed to the bottom of the dialysis cell via hole 14 and leaves this via hole 15.

During circulation of the liquids they are pumped back into the respective compartments via a supply vessel after leaving the cell. If one or more liquids pass the respective compartments only once, this is indicated in the report by the term dosing.

3. Thickness of the compartments.

During the course of the investigations the thickness of the middle compartment, originally 3 mm, was reduced to 1.4 and subsequently to 1.2 mm. The thickness of the rinsing compartments was 1.4 mm.

For carrying out a number of experiments with neutral rinsing

liquids the thickness of the electrode compartment was doubled and divided in two by a diaphragm made of saran cloth. In this case the neutral rinsing liquids pass through the spaces between the diaphragms and the membranes at a fair speed (approximately 4-8 l/h) before leaving the cell along the electrode. In this manner completely neutral liquids flow along the membranes, whilst the compounds formed by the electrode processes enter the rinsing liquids only afterwards.

4. Current density.

In the experiments described in the sections VI.B, D and E a current density of approximately 2.6 ma/cm^2 was used. The current densities used in section VI.C are stated there.

B. Experiments with non- or only slightly selective membranes.

Two series of electrodialyses under considerably varying conditions were carried out, viz., one series in which untreated cellophane was used, and one series in which the cellophane membranes were treated with bakelite or some other lacquer.

The degree of acidity or alkalinity of the rinsing liquids can be adjusted:

1. by adding acid and/or alkali to the rinsing liquids.
2. by using the formation of acid and alkali at the electrodes. This may occur in two ways:
 - a. by allowing the rinsing liquids to circulate, as a result of which an accumulation of hydrogen ions and hydroxyl ions takes place in the rinsing liquids.
 - b. by arranging for their dosing rate to be so low that the concentration of the hydrogen ions and the hydroxyl ions in the rinsing liquids is sufficient to effect desalting of the dialysate.

Neutral rinsing liquids are obtained in the manner indicated in section VI.A.3.

The lowest energy consumption for desalting from 1000 to 300 mg Cl⁻/l reached during desalting with non- or only slightly selective membranes, and thicknesses of the anodic, dialysate and cathodic compartments of 1.5, 3 and 1.5 mm respectively, was 10-11 kWh/m³ whilst for q the maximum was approximately 36 g NaCl/100 amp.hr¹); in this case q (30-20) amounted to a value of 48 (Cf. Table IX).

However, in the case of the electrodialyses carried out with untreated cellophane membranes at dosing rates of the anodic and cathodic liquid of 0.25 and 0.15 l/h respectively the anodic membranes got strongly corroded after three to four hours. For this reason the causes of this corrosion and the factors which might be able to reduce or even prevent it were investigated (see section VI.B.2). In this investigation it was found that the q-value was increased by 35-50% if in similar circumstances the electrodialyses were performed with bakelitised instead of with untreated membranes. In view of this the membranes were treated in various manners in order to effect an increase of q (see section VI.B.3), and therefore a lower energy consumption, for the above mentioned energy consumption is too high for industrial application of the process.

The various subjects referred to will be dealt with in greater detail in the following paragraphs.

1. Electrodialyses with cellophane membranes and varying acidity and alkalinity of the rinsing liquids.

Some of the experiments are referred to in Table IX in which the different circumstances under which electrodialysis was performed are recorded.

One of the points noticed about these electrodialyses was that an excessive acid and/or lye concentration of the anolyte and/or the catholyte -which would result in a lower terminal voltage- retards chloride removal from the dialysate. In Graph 10, for instance, the time and the number of ampere-hours passed through in the four experiments (1-4 incl.) are plotted against the chloride concentration of the dialysate. From this graph the favourable influence of reduction of the sulphuric acid concentration is evident. Apart from

¹) per 100 amp.hr a maximum of 218.4 grammes of sodium chloride can (theoretically) be removed.

thus the four experiments were carried out under identical conditions, which -needless to say- applies to all series of experiments compared in Graphs 10-18 incl.

2. Corrosion of the anodic membrane.

a. Detection of the corrosion.

Originally a simple method was used for detecting corrosion of the anodic cellophane membrane, viz. colouring with methylene blue. The blue alkaline dye turns dark blue those places where chemical corrosion has resulted in the formation of oxy cellulose and hydrocellulose, the cellophane itself turning only pale blue. The intensity of the blue colour is an indication of the degree of corrosion (97).

Quite soon it was decided to colour the membranes with Turnbull's blue, a colour more characteristic for the carboxyl groups formed by oxydation. The membrane is treated with ferro-sulphate and potassium ferricyanide in succession, which causes the places where so-called oxy cellulose has formed to turn dark blue whilst the other places remain uncoloured (98). Figure 5, a picture of a piece of corroded membrane dyed with Turnbull's blue, has been included in the report. This clearly shows the pattern of the membrane support.

The colouring of cellophane membranes treated with bakelite-, cresurol-, paralacquer, etc., was not practicable; moreover this might cause blueing in places other than those corroded. In the determination of the degree of corrosion of cellophane membranes, treated in some way or other, and that of membranes not made of cellophane (for instance Perminic membranes) only the mechanical strength and the surface of these membranes were examined more closely.

b. The cause and reduction of corrosion.

By means of a series of electrodialyses, performed with non-treated cellophane membranes under different circumstances the causes of corrosion and the factors influencing it were inves-

tigated. Suffice it to recount the results and some technical details.

1. Corrosion of the anodic membrane starts in the anodic compartment by the hypochloric acid which has formed at the anode.
2. The concentration of the hypochloric acid in the anolyte and the consequent corrosion of the membrane may be reduced:
 - a. by adding sodium sulphite to the anolyte,
 - b. by increasing the dosing rate of the anolyte,
 - c. by raising the acidity of the anolyte,
 - d. by aerating the anolyte,
 - e. in certain cases by increasing the current density.
3. Corrosion of the anodic membrane can be reduced by bakelitising it.
4. When an acid anodic rinsing liquid is used the life of the anodic membrane stays limited despite aeration or bakelitisation.

c. Method of aerating the anolyte.

In section III it was explained already how the concentration of the hypochloric acid might be reduced by rapid removal of the chlorine gas (for instance by aeration) and by increasing the acidity of the anolyte.

Two methods of aeration were used viz. bubbling air through the anodic compartment and aerating the anolyte outside the cell.

When air is bubbled through the anodic compartment the maximum amount of air is only small owing to the limited volume of the anolyte. Experiments proved that under the circumstances chosen (cf. experiments 5 and 6, Table IX) at least fifty litres of air had to be passed through hourly in order to prevent corrosion during one electrodialysis experiment. Industrial use demands such a long life that larger quantities of air are required which cannot be bubbled through the cell without major difficulties.

Aeration outside the cell produces better results as it enables larger quantities of air to be used without any difficulty. The anodic rinsing liquid drips into the top of a tower filled with glass beads or Raschig rings, the air being fed into the bottom of the tower at a rate of hundred litres per hour. This ensures thorough desorption

of the chlorine. This method of aeration, unlike the before mentioned, is effective only if a circulating anolyte is used. The circulation rate should not be too low as this would cause the concentration of active chlorine contained in the anolyte to rise too much and corrosion still to occur.

d. Bakelitising the membranes.

The membranes were dipped in various concentrated ethylalcoholic and isopropylalcoholic solutions of a condensation product of phenol and formaldehyde (bakelite lacquer; dry matter: 48%). Thereupon, in order to evaporate the solvent, they were dried for a few hours and subsequently bakelitised by heating at 100°C. The baking and drying times producing the best results were determined experimentally. In doing so chlorine resistivity and mechanical properties had to be taken into account. 10% solutions, both in ethyl- and in isopropyl-alcohol yielded the most stable membranes. Since, however, moistening left much to be desired in the first case, only the second solvent was considered suitable. Drying for two hours at 60°C and baking at 100°C for seven hours yielded the best results.

In Graph 11 two examples are given of electrodialyses (exp. No. 7, 8) carried out with bakelitised membranes under circumstances referred to in Table IX. The value of q was approximately 36 and for q (30-20) a value of 48 was obtained, whilst the electrodialysis experiment 9 with non-treated cellophane membranes, but otherwise performed under the same conditions, produced a q -value of 27.

In the experiments 7 and 8 the value of the energy consumption (N_E) amounted to approximately 13 kWh/m³.

3. Enhancing the selectivity of the cellophane membranes by treating them with different lacquers.

A series of electrodialyses with different membrane combinations was performed, and for each desalting the q -values as well as some charge efficiencies of the membranes were calculated. The following membranes were used:

non-treated cellophane membranes,
cellophane membranes impregnated with bakelite lacquer, cresurool
lacquer or para lacquer;
cellophane membranes impregnated with A.F.-lacquer made by the
Fibre Research Institute T.N.O.,
cellophane membranes treated with hypochlorite (indicated by cell.
ox.).

In these experiments the rinsing liquids (0.03 n sodium chloride
solutions) were dosed at fairly high rates (4-6 l/h, Cf. Table X). By
application of the method described in section VI.A.3 it was ensured
that the pH of the rinsing liquids did not deviate much from 7.0, so
that the membranes were tried in almost neutral solution. Data relating
to some of these experiments are summarized in Table X.

a. Lacquer treatment of the anodic membrane.

Graph 12 clearly indicates the favourable influence of treating
the anodic cellophane membrane with bakelite lacquer (Cf. exp. No
12 and 13; and see also exp. No. 7, 8 and 9 in Graph 11). The effect
of treatment with cresurool- and para-lacquer is equally favourable
to q , viz. it roughly doubles it, whilst treatment with A.F.-lacquer
does not materially improve the result (Cf. exp. 12 and 16). The
increase in the average terminal voltage is - 0.1, 0.6, 3.4 and 10.8 v
for membranes treated resp. with A.F.-lacquer, bakelite-, cresurool-
and para-lacquer.

Since the membranes treated with cresurool lacquer are less
supple than bakelitised membranes and in addition they absorb less
water, the most favourable results in many respects have so far
been achieved by bakelitising the anodic membrane.

b. Treatment of the cathodic membrane with lacquer.

If we compare the curves of desalting experiments 17 and 18 in
Graph 13, the favourable effect on q of a careful treatment of the
cathodic membrane with hypochlorite and boric acid, which treatment
result in slight oxydation, will be clearly observed. The effect of
impregnating the cathodic membrane with A.F.-lacquer (experiment
No 19) on q is not very great.

From this series of experiments in which rinsing was done with
neutral liquids, the detrimental effect of this rinsing on the de-
salting was obvious, when the membranes were but slightly selective.

In order clearly to demonstrate this influence Graph 14 was
plotted.

For experiments 11 and 17 the number of ampère-hours passed through
is plotted against the sodium chloride concentrations of the dialysate.
In both cases the same membrane combination was used. The values for
 q (30-20) were 48 and 24 g NaCl/100 amp.hr. resp. The only difference
was the use of acid and alkaline rinsing liquids in experiment No. 11
and of neutral ones in experiment No. 17.
In experiments 9, 10 and 12, in which two non-treated cellophane
membranes were used, the rinsing liquids were dosed at identical
rates. In experiment 12 however, the rinsing method with neutral
rinsing liquids was adopted. In this case the desalting process
took almost four times as long (Cf. Graph 14).

4. The charge efficiencies in the membranes.

In a number of experiments the charge efficiencies of the chloride-
ion in the anodic and in the cathodic membrane were calculated, in ac-
cordance with the method described in section V.E. They are given in
Table XI.

5. The results of the experiments with non- or only slightly-
selective membranes.

The principal results of the experiments are:

An energy consumption of less than approx. 10 kWh/m³ for the
desalting with the use of non-selective membranes from 1000 to 300
mg Cl⁻/l was not obtained. The q -value is then roughly 36 g NaCl/100
amp.hr¹), and q (30-20) approx. 48 g NaCl/100 amp.hr.

Even when the membrane is bakelitised or the anolyte is aerated,
the life of the anodic membrane stays limited.

Excessive acid and/or lye concentrations of the anolyte or ca-
tholyte retard the removal of chloride from the dialysate.

The use of neutral rinsing liquids strongly retards the desalting
effect in experiments with non- or only slightly selective membranes.

¹) theoretical maximum of $q = 218.4$ g NaCl/100 amp.hr.

When non- or only slightly selective membranes are used q declines sharply as the sodium chloride content of the dialysate decreases.

As a result of different treatments of the membranes the q -values are increased by 35-50%. From the point of view of increased terminal voltage the bakelitised membranes gave the best results.

Summarizing we can say that, though by various methods an improvement in energy consumption was achieved, it remained unattractive for industrial use. Since already very thin cells were used, further experiments were directed especially towards an increase in the selectivity of the membranes.

C. Research into the usefulness of selective membranes for electrodialytic desalting of water.

In the course of the investigation several Permionic membranes were placed at our disposal, viz: membranes of the types CR 51, ARX 44 and ARX 102, consisting of a layer of cation or anion exchanger on a diaphragm made, for example, of nylon gauze or paper. The Fibre Research Institute T.N.O. made moreover a number of excellent selective membranes on a cellophane basis ¹⁾, including the types A 17b, A 19, A 21, A 22¹, and A 40.

In the following sections we will describe research into several of these membranes, as to their physico-chemical and mechanical properties and their selectivity on the passage of current. At first we only got samples which were too small for the electrodialysis apparatus normally used. Special small electrodialysis cells (A 1 and A 2) were built for the experiments with these samples. In these cells the middle compartments were 6 and 31 mm thick respectively and carbon electrodes were used. Where the experiments described were performed in the small cells, this will be stated. The experiments without any such indication were carried out with larger membranes (subsequently obtained) in the three-compartment cell we normally used, in which the thickness of the middle compartment was further reduced in size

¹⁾ Suggestions on the preparation of these membranes were made by Drs H.G. Roebersen.

to 1.2 mm, while the thickness of the rinsing compartments was 1.3 mm.

1. Physico-chemical properties.

Table XII contains some data on the physico-chemical properties of these membranes, i.e. with regard to their properties in a "state of rest".

Membrane ARX 44 proved unsuitable for technical use on account of its high resistance.

2. Mechanical properties.

If membranes are to be suitable for technical use they must satisfy certain mechanical requirements, and consequently this aspect was also considered.

Generally speaking, the mechanical properties of the Permionic membranes are not good. They are fairly rigid plates, measuring 20 x 20 cm, which have to be kept under wet conditions to prevent cracking. Membrane ARX 44 had cracked after being kept some time under wet conditions and in this respect it is unsuitable for industrial use. Furthermore these membranes, unlike cellophane membranes, have the great drawback for use in thin electrodialysis cells that they are no longer absolutely flat after some time.

The T.N.O.-membranes were much better and quite usable as regards their mechanical properties.

3. Selectivity on passage of current.

In cells A 1 and A 2 the influence of the current density and of intensive agitation (agitation and/or circulation) of the dialysate on q was investigated. The results of these investigations are shown in the Graphs 15 and 16, and in the Tables XIII and XIV. At greater current densities q appeared to decline, while this fall began only later if care was taken to ensure intensive movement of the dialysate.

The explanation of this association is easy to find. With highly selective membranes, close to the membrane, thin films of a greatly deviating sodium chloride concentration are formed. Desalting will take place more rapidly if these films are mixed more

rapidly with the other liquid. The greater the current density used, the quicker such films are formed again, i.e., the more intensive the agitation required. The decline caused by this agitation is greater with the use of the membrane combination ARX 102 - CR 51 than with the use of the combination A 19 - CR 51. This is perhaps caused by the rougher surface of the membrane ARX 102, as a result of which the film close to the membrane surface is perhaps less easily disturbed.

The presence of films of greatly differing concentrations close to the membranes (Cf. Bethe-Toropoff) is proved by the measurement of the pH's close to the membranes. In a certain informative test (current density: 4 ma/cm²; membranes A 19 and cell ox.), the following pH's were measured at a certain moment:

anode	anodic membrane	cathodic membrane	cathode
6	11 3.5	7 7.5 3.5	9

As an example of the results that can be obtained with the use of selective membranes, we give now a description of experiment No. 49.

The membranes used were T.N.O.-membranes A 21' and A 22', the current density 2.6 ma/cm² and the thickness of the three compartments 1 mm. The circulation rate of the dialysate was 13 l/h, the dosing rate of the rinsing liquids 5 l/h (see Appendix 8).

The energy consumption for desalting from 30 to 9 meq.Cl⁻/l was 3.3 kWh/m³, which by interpolation¹⁾ gives an energy consumption for desalting from 28 to 8 meq. Cl⁻/l of 3 kWh/m³. The q(30,9)-value attained was 180 g NaCl/100 amp.hr i.e. 82% of the (theoretical) maximum. Desalting took 55 minutes, the terminal voltage rose from 4.5 to 5.5 v, and averaged 4.8 v.

¹⁾ The interpolation or extrapolation of desalting ranges is not strictly allowed. If, however, ranges are desalinated which like the above mentioned range differ very slightly from the desalting range normally used 28 to 8 meq. Cl⁻/l the difference has been shown - by experience with these selective membranes - to be too slight to cause major errors in the results found.

By means of a number of experiments it was ascertained how in this experiment the average terminal voltage of 4.8 v. was constituted.

- a. The cell filled with a 0.03 n sodium chloride solution, without membranes and without middle compartment gave a terminal voltage of 3.7 v with the current density used.
- b. From a relation established experimentally between terminal voltage and current density it follows that the voltage drop at the electrodes may reasonably be taken 3 v.

Hence the voltage drop of 4.8 v in a single three-compartment cell can be divided as follows:

voltage drop at electrodes	3.0 v
voltage drop in rinsing compartments	0.7 v
voltage drop in middle compartment and two membranes	1.1 v
terminal voltage	4.8 v

4. Influence of the acidity of the rinsing liquids.

The electrodialytic experiments 50 and 51 carried out with T.N.O.-membranes clearly show the favourable effect of the use of neutral rinsing liquids, in contrast to those carried out with slightly or non-selective membranes. The surveys of these electrodialytic experiments are given at the end of this report (Appendices 9 and 10).

The normal rinsing method, in which the liquids flow directly along the membranes and the electrodes, was used. In comparison with experiment 50 the dosing rates of the anodic and cathodic rinsing liquids were considerably higher in experiment 51 (0.3 and 1 l/h in No. 50 and 7 and 8 l/h in No. 51 resp.) and therefore the acidity and alkalinity of these liquids were only very low. The hydrogen ion and hydroxyl ion concentrations of the drawn-off rinsing liquids were 3 and 4 meq/l in No. 51, while they were 38 and 30 meq/l in No. 50. The influence of these less acid and alkaline rinsing liquids on the values of $q(c_a, c_K)$ was great: these values were viz. 99 and 173 g NaCl/100 amp.hr resp.

In experiment 51 the energy consumption interpolated¹⁾ to the normal desalting range, was 3.1 kWh/m³. The average terminal voltage in experiment 51 was 0.1 v higher than in experiment 50.

In experiment 50 $\varphi_{an}(30,8)$ and $\varphi_{cm}(30,8)$ were calculated. They were 50% and 5% respectively (Cf. the values given in Table XI).

5. Extent of diffusion.

At lower current densities the counteraction of diffusion is generally speaking, greater. This diffusion is however relatively smaller as the membranes are more selective. This is also shown in Table XV; the experiments represented were carried out in the small cells A1 and A2.

The quantity of sodium chloride was determined which after a certain course of time had diffused to the middle compartment, when it was filled with distilled water, whereas the chloride concentrations of the liquids in the rinsing compartments were kept at approx. 0.031 n. Various combinations of membranes were used.

The results show that diffusion through selective membranes per unit of time is about one-tenth that through cellophane.

6. Results.

The results of research into the usefulness of selective membranes for electrodialytic water purification can be summarised as follows:

In a single three-compartment cell with a short distance between the electrodes and with the use of selective membranes an energy consumption of about 3 kWh/m³ can be attained for the lowering of the chloride concentration from 28 to 8 meq/l.

Over 60% of the loss of energy in the said apparatus occurs at the electrodes.

With the use of properly selective membranes, q-values of 180 g NaCl/100 amp.hr, i.e. 82% of the (theoretically possible) maximum can be attained.

¹⁾ See note pg. 90.

The use of neutral rinsing liquids is necessary to attain the above mentioned q-value.

With greater current densities q declines. This decline is dependent upon the membranes used and upon the degree of movement of the dialysate.

The diffusion of sodium chloride through a selective membrane is much less than through a non-selective one.

D. Tentative experiments on chloride removal at the anode in a two-compartment cell with non-reversible electrodes.

Several desalting experiments were carried out in an electro-dialysis cell converted into a two-compartment cell (description of section VI.A.1).

The diaphragm used was a cellophane membrane in order to prevent any flow of liquid between the two compartments. In principle of course, glass fibre cloth, saran cloth and the like, can be used as diaphragms, while moreover a negatively charged diaphragm would prevent the movement of anions towards the anode (Cf. section II.A).

Unlike the desalting of the dialysate in a three-compartment cell the desalting now is only brought about by electrode processes (Cf. section III.F), viz. formation of chlorine at the anode. Therefore the removal of chloride ions in a two-compartment cell is very dependent on the nature of the anode. When the chlorine is rapidly carried off the active chlorine content in the anolyte will not grow high.

In a number of tentative experiments only the influence of the pH and the chloride content of the anolyte were examined. To this purpose diluted solutions of sodium chloride, circulating through the anodic compartment (circ. rate 6 l/h) were desalinated for one hour. The experiments were carried out at constant chloride concentrations (30, 20 and 10 meq Cl⁻/l respectively) and at constant pH's (about 1.7, 5.0 and 7.0) of the anolyte. A solution of sodium hydroxide (20 meq/l) was dosed in the cathodic compartment (dos. rate 0.15 l/h). From these experiments one could calculate the number of grammes of sodium chloride removed per 100 amp.hr in desalting at a definite constant chloride content (therefore indicated by $q(c_p)$). The main details and results

of these, only tentative, experiments are comprised in Table XVI.

The results show that under the circumstances chosen a $q(c_p)$ -value of 90 g NaCl/100 amp.hr -i.e. about 40% of the theoretical maximum- can be attained ¹⁾, and that $q(c_p)$ increases:

- a. with an increasing chloride content of the anolyte,
- b. with a higher acidity of the anolyte: this increase is larger at a lower chloride content.

c. by aerating the circulating anolyte.

As the nature and the roughness of the anode surface and the current density have a considerable effect on chlorine formation at the anode, it seems probable that the value of 90 g NaCl/100 amp.hr can be increased still further by operation under optimum conditions.

E. Several desalting experiments on potassium chloride solutions in a two-compartment cell with reversible silver-silver chloride electrodes 2).

1. Method.

The electrolysis cell is built up of two halves of plexiglass with milled out excavations measuring 10x10x0.2 cm. These depressions contain two silver-silver chloride electrodes (10x10x0.1 cm) which were thoroughly ungreased beforehand, while in addition to this the cathode had been anodically chlorinated for an hour at a current density of approx. 2.5 ma/cm² in a 4% potassium chloride solution. Theoretically therefore this electrode can now function for one hour as a reversible electrode, if a current density of approx. 2.5 ma/cm² is used. In practice however, it proved to be usable for half an hour.

The current supply to the electrodes is effected through perforations in the plexiglass; the liquids are fed and run off through three holes in the top and three holes in the bottom of each half cell.

¹⁾ Cf. experiment no. 54.

²⁾ These experiments were suggested by Prof. Dr J.Th.G. Overbeek.

The two cell halves are separated by a cellophane membrane 0.02 mm thick, while for the various experiments they were filled with solutions of potassium chloride pro analysis, with concentrations varying between 28 and 14 meq Cl⁻/l. These liquids were circulated during electrodialysis by pumping at speeds of 0.9 - 72 l/h.

When current passes silver chloride is formed on the anode and the anodic liquid is desalinated. On the cathode on the other hand silver chloride is converted into silver, and in the cathodic compartment salt accumulation occurs. By reversing the polarity from time to time and simultaneously interchanging the two liquids, continuous desalting of one of these liquids was obtained.

Determination of the chloride concentrations was effected conductimetrically as there were no other salts in the solution and the pH remained in the region of the neutral point, viz. between 7 and 6.7 for the cathodic liquid and between 7.0 and 5.7 for the anodic liquid.

2. Results of the experiments.

a. Energy consumption and desalting effect.

The results of a number of experiments are given in Table XVII. As the desalting did not cover the range from 28 to 8 meq Cl⁻/l on any occasion, we shall try to deduce the order of magnitude of the kWh consumption per m³ from the experiments.

It appears that for the ranges 27-17 meq Cl⁻/l and 19-6 meq Cl⁻/l the average amounts of energy needed for a decrease in concentration of 1 meq Cl⁻/l and expressed in kWh/m³ are 0.06 and 0.04 respectively. Now the energy consumption for desalting from 27-6 meq Cl⁻/l is taken to be composed of the amounts corresponding to the steps 27-18 and 18-6 meq Cl⁻/l. Hence it becomes:

$$9 \times 0.06 + 12 \times 0.04 \approx 1.0 \text{ kWh/m}^3$$

Extrapolation to the range 28-8 meq Cl⁻/l yields approximately 1 kWh/m³ and a desalting time of 3½ hours for 500 ml.

We have applied this method of calculation and have not extrapolated the result of every experiment directly to the

desalting range 28-8 meq Cl^- /l as extrapolation is not allowed, if it has not first been proved that the degree of desalting is independent of concentration. The extrapolation now applied by us is done over a very small range.

For potassium chloride solutions q -values can be attained of 132 g KCl /100 amp.hr, which would correspond to $q_{\text{NaCl}} = 103$ g NaCl /100 amp.hr. This conversion is not entirely correct as the transference numbers of sodium and potassium ions are not the same. Nevertheless they do give an idea of the magnitude of q if sodium chloride solutions had been desalinated.

b. Trend of voltage and adhering of silver chloride.

As the starting voltage of 0.3 v rapidly increased in these experiments (cf. Graph 18) it was necessary to limit this as far as possible-so as to keep down energy consumption- and not allow it to exceed a certain value. Therefore, as soon as the voltage exceeded this value reversion of polarity was applied.

The voltage increases in consequence of worsened adhering to the electrode of the silver chloride formed at the anode. Adhering appeared to be better when:

the silver plates are thoroughly degreased before anodic chlorination;

a network of grooves with 1 x 1 mm squares and 0.5 mm deep is scratched in the electrodes;

the silver chloride layer is thinner. If greater current densities are used the intervals between the reversal of the polarity must be much smaller in order to keep the voltage below the above-mentioned value. With lower current densities however the counteraction of diffusion will always be greater: the voltage can be kept constant for longer periods by higher rates, but an increase cannot be suppressed.

reversal of the polarity is less frequent; the oftener it is done, the shorter the interval between two reversions will have to be (Cf. e.g. exp. 65, Table XVII and Graph 18).

c. Membranes.

Particularly with higher rinsing rates it is very difficult to prevent contact between the cellophane membranes and the electrodes. With the use of thicker membranes (e.g. 0.09 mm) with the aim at retarding the diffusion, it is practically impossible to avoid this contact without using membrane supports.

d. The silver content of the water.

The quantity of silver ions in the desalinated solution was not determined, so it is not known whether the desalinated product is suitable as drinking water.

e. Results.

The results can be summarised briefly as follows:

In a two-compartment cell with reversible silver-silver chloride electrodes, desalting of half a litre of water from 28 to 8 meq Cl^- /l can be achieved with an energy consumption of approx. 1 kWh/m³, provided various measures are taken to make adhering of the silver chloride as good as possible. This desalting takes about 3½ hours.

Silver-silver chloride electrodes will probably not stand up to regular use, and with desalting as above the cost of electrodes will be considerable.

F. Discussion of the results.

1. Experiments performed with the two-compartment cells.

With regard to the results of these experiments it should be pointed out that industrial use of the two-compartment cell with non-reversible electrodes for desalting water with high chloride concentration (e.g. sea water) is justified. The suggestion is attractive, since no heavy demands are made upon the membranes or diaphragms. Further research in this direction is very desirable.

Desalting in a two-compartment cell with reversible electrodes opens up possibilities only if redox-electrodes can be found, of which the operating costs are not excessive. This is not so for silver-silver chloride electrodes.

2. Experiments performed with the three-compartment cell.

Desalting with the use of non- or only slightly selective membranes and more or less acid and/or alkaline rinsing liquids will not be considered owing to the low q -values and the consequently high energy consumption. Desalting with the use of selective membranes offers better prospects, at least for desalting brackish water.

On the assumption of a kWh price of Fl. 0.07 an energy consumption of 3 kWh/m³ for desalting water from 1000 mg Cl⁻/l to 300 mg Cl⁻/l still leads to a cost of Fl. 0.21/m³ for energy only. The cost of apparatus, operation etc. are roughly estimated to amount to approximately six times the above mentioned value. The greater part of these costs is formed by the cost of the magnetite anodes and the membranes. Thus we arrive at the conclusion that the total costs will amount to approximately Fl. 1.50/m³ desalinated water.

In view of the average price of potable water in the Netherlands viz. Fl. 0.20 - Fl. 0.15/m³ it will be clear that industrial desalting in a single three-compartment cell is not economically justified.

The factors determining energy consumption have been dealt with at length in section IV. A low terminal voltage as well as a high q -value are necessary for ensuring a low energy consumption. Under conditions which are also industrially practicable high q -values have already been attained, viz. up to 82% of the theoretical maximum. A substantial further reduction of the energy consumption by reducing the current density is not possible, so that the only solution is to reduce the effect of the terminal voltage factor on energy consumption.

The terminal voltage can be reduced to a limited extent by working with thin compartments. From the results shown on page 91. it appears that more than 60% of the terminal voltage is due to the overvoltage at the electrodes. If reduction of this percentage were possible, energy consumption of less than 3 kWh/m³ could be achieved. According to data in the literature roughening the electrode surface would result in a decrease of the overvoltage of approx. 0.5 v i.e. in a 10% reduction in energy consumption. However, even this amount is too small.

The only remaining possibility is increasing the number of dialysate compartments per set of electrodes. If between two electrodes one more unit consisting of two membranes, a dialysing and a rinsing compartment is interposed, the total terminal voltage according to the data on pag. 91, becomes $4.8 + 1.45 = 6.25$ v. The portion accounted for by overvoltage is thus reduced to 48%.

Supposing a total of hundred of these units per cell, then the portion of the voltage drops at the electrodes is only 2%, whereas for two hundred units it becomes 1% per cell. With the compartment thickness and current density given in experiment 49 (see Appendix 8) there would be no point in reducing energy consumption per m³ by using more than 200 units per cell. With such an arrangement the number of magnetite anodes required will be reduced considerably viz. by a factor 100 or 200. In addition the greater part of the membranes will not be exposed to the corroding influence of extreme pH-values and/or chlorine, which involves a longer life of the membranes. Hence the cost of apparatus, etc. will be considerably lower than the preliminary estimate made on pg 98 for the case of single three-compartment cells. The possibility of economically realising electrodialytic desalting of water in a multi-compartment apparatus therefore seems to exist. For this reason we give below an approximate calculation of the cost price of water thus obtained for a capacity of 48,000 m³ per day, which is about one tenth of the Netherlands' estimated requirement in drinking water in the year A.D. 2000.

3. A tentative calculation of the cost price of electrodialytic desalting of brackish water from 1000 to 300 mg Cl⁻/l for a capacity of 48,000 m³ per day in a multi-compartment apparatus with the use of selective membranes and magnetite anodes.

The following calculation is based upon the conception of a multi-compartment apparatus, subdivided into cells, units and compartments (cf. Fig. 6). In accordance with Fig. 6 the smallest items are the compartments. Each unit consists of one rinsing compartment and one dialysate compartment, inclusively two membranes (one positively charged and one negatively charged). A set of units together with two electrodes and one extra rinsing compartment constitutes a

cell. The total apparatus consists of a number of such cells.

In the calculation the number of units per cell is chosen at 200, whilst data of experiment 49 (Cf. Appendix 8) are used.

a. The required cell area.

The required cell area may be estimated if it is assumed that as in experiment 49 a q -value of 180 g NaCl/100 amp.hr can be attained. In this test the effective cell area is 580 cm^2 .

From the data a capacity of $\frac{60}{55} \times 2 = 2.18 \text{ l/h}$ is found.

The following area of each membrane species (positive and negative) is therefore required for a capacity of $48,000 \text{ m}^3$ per day

$$\frac{48,000,000}{24} \times \frac{1}{2.18} \times 0.0580 \text{ m}^2 = 53,500 \text{ m}^2.$$

The maximum width of the cell area is for the time being determined by the maximum obtainable width of cellophane, so that it cannot exceed 0.40 m. The height of the cells will probably be chosen in such a manner as to ensure that desalting is effected in only one pass through the compartment, provided the further consequences thereof -such as concentration differences within the compartments, etc. -are acceptable, which would have to be determined later. For a capacity of 2.18 l/h the circulation rate was 13 l/h for a cell height of 30 cm . In order that a single passage would suffice a cell height of $\frac{13}{2.18} \times 30 \text{ cm} = 1.80 \text{ m}$ or, say, 2 m would be needed.

The effective cell area thus becomes $2 \times 0.4 = 0.8 \text{ m}^2$ and the total number of units $\frac{53,500}{0.8} = 67,000$, which in the case of 200 units per cell amounts to 335 cells. This number of units per cell applies only to the membrane spacing used in the experiment. In the case of smaller membrane spacing the number of units per cell will have to be larger so as to attain the same percentage of voltage losses at the electrode per unit.

b. The cost of the membranes.

The low current density applied is one of the reasons why a very large membrane area is required. For an effective cell

area of $200 \times 40 \text{ cm}$ one should allow for a gross membrane area of, say $230 \times 50 \text{ cm}$.

For 67,000 units a length of $67,000 \times 2.30 = 154,000 \text{ m}$ is required for each of the two kinds of membrane, i.e. a total of $308,000 \text{ m}$. At a cost of Fl. 75.- per 100 m this involves an expenditure of Fl. 231,000.- excluding the costs of preparing the membranes. If we estimate these costs at say Fl. 0.25 per straight metre, we arrive at Fl. 77,000.- for the aforementioned $308,000 \text{ m}$. The total costs for one set of membranes then amount to a rounded-off figure of Fl. 310,000.-.

Hence it follows that the life of the membranes is a vital factor in the cost-price of the water, since the membranes' portion of the total costs, at the current density selected, becomes acceptable only if a prolonged life is ensured. This fact is clearly demonstrated in the following table:

Life of membranes	Total production of desalinated water in m^3	Total costs of the membranes	Costs of the membranes per m^3 desalinated water
1 week	336,000	Fl. 310,000,-	Fl. 0.93
4 weeks	1,344,000	" 310,000,-	" 0.23
24 weeks	8,064,000	" 310,000,-	" 0.04

c. Energy consumption.

The current strength required per cell for a current density of 2.6 ma/cm^2 and a cell area of 8000 cm^2 works out at 21 amps.

The terminal voltage per cell averages $(200 \times 1.45) + 0.35 + 3 = 295 \text{ v}$. Per cell a direct current power averaging 6.2 kW is taken up. The total direct current power for 335 cells becomes 2080 kW , so that energy consumption of the desalting amounts to $\frac{2080}{48,000} \text{ kWh/m}^3$ or just more than 1 kWh per m^3 .

- 102 -

d. The costs of the magnetite electrodes.

For the manufacture of flat magnetite electrodes a price of Fl. 200.— per m^2 magnetite area is reckoned (this refers to the combined area at both sides).

By combining two cells the area on both sides of the magnetite anodes can be used. The total anode area is $335 \times 0.8 m^2 = 268 m^2$. The price of a complete set of anodes is therefore Fl. 54,000.—. With a life of 24 weeks the magnetite costs are 0.68 Dutch cents per m^3 .

The price of the iron cathodes is neglected

e. Energy consumption by the pumps.

Assuming that the total amount of water has to be pumped to a height of 10 m, with an overall pump plus motor efficiency of 50%, the consumption per m^3 is 20,000 kgm or 0.06 kWh/ m^3 .

f. Wages operators.

This cannot yet be estimated. On the assumption that 20 men will be required for one shift, the total is 60 men at hourly wages of Fl. 1.25 and an eight hours' working day. Add to this an overhead of 200% for management, administration, workshops, social insurance etc. and the total amount of daily wages becomes $\frac{300}{100} \times 60 \times 8 \times Fl. 1.25 =$ = Fl. 1800.—. These costs thus amount to 3.75 Dutch cents per m^3 .

g. Depreciation costs.

At this stage the capital investment cannot be specified, since the correct design of the apparatus, for instance, has not been finally determined. However, to get some idea of the extent of the various items, it seems reasonable to assess the total capital investment on installation, buildings, laboratory, etc. at Fl. 3,000,000.—. Calculating on the basis of 10 years' depreciation the costs of depreciation for an annual production of 17.5 mill. m^3 water is 1.7 Dutch cent per m^3 .

h. Maintenance of the installation.

Allowing for an annual amount of Fl. 50,000.— for maintenance of the installation, incl. lubricants, maintenance and cleaning material, this works out at roughly 0.3 Dutch cent per m^3 .

- 103 -

i. Summary of the cost price factors discussed.

In the preceding sections the principal factors determining the cost price of desalting brackish water have been dealt with. Many of these amounts will be found in the following table, which is based on the assumption that electric power can be obtained at Fl. 0.07 per kWh.

Survey of operating costs and calculating of cost price per m^3 water
(Annual production 17.5 mill. m^3 water)

Costs for	Fl. per year	Dutch cents per m^3	Percent of total costs
Electric energy:			
Direct current			
18.2 mill. kWh	1,275,000.—	7.28	1
Power 1.05 mill. kWh	73,500.—	0.42	
Membranes (4 weeks)	4,030,000.—	23.—	6
Magnetite (6 months)	116,000.—	0.68	
Wages	656,000.—	3.75	1
Maintenance	50,000.—	0.29	
Depreciation	300,000.—	1.72	
Total	6,500,500.—	37.14	100

The cost price accordingly amounts to Fl. 0.37 per m^3 before the advantage over the use of a single three-compartment is obvious. In the latter the cost price amounts to Fl. 1.50 (Cf. pg. 98).

The costs of the magnetite anodes are no longer of importance. With regard to the cost of maintenance, and to some extent depreciation, it is obvious that they do not yet affect the costs.

Obviously membrane and energy costs constitute the largest items, and any further reduction of the already attractive cost price has to be sought by reduction of these costs.

- 104 -

The membranes account for more than 60% of the cost price, so that we wonder whether it might be possible to operate with greater current densities which would enable the membrane area to be reduced. On the other hand in that case the energy consumption will be higher. However, further reduction of the width of cells might bring down energy consumption. Further reduction of membrane costs is possible if they are given a longer life and are made of a less expensive base material.

As to the reduction of energy costs it should be pointed out that the figure given for direct current energy - 1 kWh per m^3 - is based on previous experimental results and hence can be considered reliable. Needless to say the most important feature is the industrial production of membranes which keep their original selective properties even when they are used for longer periods. This subject has hardly been examined yet, which is also the case with the construction of the multi-compartment electrodialysis apparatus on an industrial scale.

The price of a kilowatthour is also of great importance. Where they are available at low prices, it would be more economical to use more kWh's and a smaller membrane area (higher current density). It is thought that minimum total costs will be realised if membrane and power costs are roughly equal.

- 105 -

BRIEF SUMMARY.

The problem of water supply, already existing in some countries and imminent in other countries, is responsible for the fact that many countries are actively seeking an economical method of preparing water for domestic, industrial and agricultural use from sea or brackish water.

The principal existing methods have been examined and their costs have been compared. In addition a number of surveys have been made of patents relating to these methods.

The various investigations and calculations appertaining to electro-dialytic desalting of water and the ensuing processes at the electrodes have been thoroughly examined.

As the energy consumption appeared to be a vital economic factor all elements governing energy consumption in electrodialysis have been thoroughly studied.

Of major importance in this respect are the charge efficiencies in the various membranes of the ions to be removed. With the aid of theoretical considerations it has therefore been ascertained what conditions affect these efficiencies.

In view of the prevailing confusion definitions have been suggested of current-, current strength-, current density-, charge- and coulomb efficiencies.

Experimental research has been performed into the electrodialytic desalting of water in a single three-compartment cell by means of non-selective and more or less selective membranes, with the use of acid, alkaline or neutral rinsing liquids.

In addition a number of experiments has been carried out concerning desalting in a two-compartment cell apparatus with non-reversible electrodes and with reversible silver-silver chloride electrodes.

With the help of the results obtained the construction of a multi-compartment apparatus with selective membranes has been recommended, and a tentative cost calculation has been made for a capacity of 48,000 m^3 desalinated water per day.

According to this calculation it appeared possible to desalt 1 m^3 water from 1650 to 500 mg sodium chloride per litre at a cost of Fl. 0.37 per m^3 , while further reduction of this figure seems possible.

- 107 -

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Seawater reclamation costs (1, 2, 8)

Method	Costs ¹⁾ for			
	Diesel fuel oil		Power 2 cent/kWh	Chemicals (South California)
	9.5 cent/l 200:1 ²⁾	11.7 cent/l 220:1 ²⁾		
Vapour com- pression distillation	54	63 ⁴⁾		125
Freezing out				125
Ion-exchange				2500
Electrolytic process of Briggs ⁵⁾			90	

¹⁾ The cost is shown in Dutch cent per m³ produced water. Prices of "raw materials" are given in the table in various columns.

²⁾ Water to fuel ratio (see text).

³⁾ Cost at sea level, excluding cost of distribution. Allowing for pumping from sea level, labour, interest, amortization, road factor, distribution and so forth, the actual average cost might total more than three times the bare fuel, power or chemical costs.

⁴⁾ This figure originates from Leicester (8)

⁵⁾ See section II.A.4.a.

Plev.
27-9-1952.

A.T.A.-T.N.O.
T.A. No 270.
Table I.

Comparison of operating costs of vapour compression distilling units and conventional steam heated evaporators¹⁾ (1,8)

Costs of	steam evaporators				vapour compression stills	
	single effect	double effect	triple effect	quadru- ple eff.	electrical drive and heating	diesel drive with exhaust heat exchangers
steam, based on cost of steam at 0.9/kg	1079	555	388	304	21	21
condenser water, based on cost of water at 26/m ³	84	42	26	21	-	-
electric power, based on cost of power at 4,4/kWh	12	8	8	8	73	
fuel, based on cost of fuel at 9.5/l (1:200) ²⁾ . id. at 11.7 l(1:220)						54 ⁴⁾ 63
water and energy	1175	605	422	333	94	84
total costs ³⁾						125 ⁴⁾

¹⁾ See note 1, table I.²⁾ See note 2, table I.³⁾ See note 3, table I.⁴⁾ These figures originate from Aultman (1)A.T.A.-T.N.O.
T.A. No 270.
Table II.

The mobility of different ions at 25°⁰C and at
a voltage drop of 1 volt/cm, expressed in 10⁻⁴ cm.sec

H ⁺	36.2	OH ⁻	20.5
K ⁺	7.6	Cl ⁻	7.9
Na ⁺	5.2	SO ₄ ²⁻	8.3

(Increase $\pm 2\%$ per °C rise in temperature)

The hypochloric acid concentrations in
the anolyte for various conditions.¹⁾

pH	[Cl ⁻] in n	p in atm.	[HClO] in 10 ⁻² n
2	0.1	1	2.150
2	0.1	0.1	0.215
2	0.000001	0.0001	2.150
1	0.000001	0.0001	0.215
2	0.03	0.0001	0.000072
7	0.03	0.0001	7.2

¹⁾ See calculations section III.B.2

A.T.A.-T.N.O.
T.A.No 270
Table III, IV.

The electrodialytic desalting of water with application
of a hydrostatic pressure difference (36)

Conditions	Water rich in carbonate and sulphate	Carbonate-, sulphate- and chloride-contain- ing water
Average voltage per cell (v) ¹⁾	13.75	13.75
Current density (ma/cm ²)	0.5	1.5
Hydrostatic overpressure (mm head of water)	26	58
Diaphragms	linen	linen
Quantity of water moved per hour through the diaphragms (l)	0.58	1.6
Quantity of water purified per hour (l)	10	10
Dry residue of the water(mg/l) untreated	159	620
Dry residue of the water(mg/l) treated	9	8
Energy consumption (in Wh/m ³ /mg salt)	44	32
		18 1.5 200 ceramics 25 10 1320 free of chloride 124 37

¹⁾ According to Billiter a potential difference smaller
than 20 volts is generally most favourable, preferably
between 8 and 16 volts.

A.T.A.-T.N.O.
T.A.N°270.
Table V.

The potential of magnetite electrodes in some solutions according to Wells (88)

solution of	pH	potential (v)
sulphuric acid (1 n)	± 0.3	+ 0.91
potassium chloride (5%)	± 6.5	+ 0.40
sodium hydroxyde (1 n)	± 14	- 0.22

EMF of some cells with a magnetite electrode according to Tammann (89)

cell	EMF (v)	$E_{Fe_3O_4}$ (v)
$Fe_3O_4/ZnSO_4$ soln. 4n/Zn	+ 1.20	+ 0.40
$Fe_3O_4/PbCl_2$ soln. satd./Pb	+ 0.60	+ 0.41
$Fe_3O_4/CuSO_4$ soln. 2n/Cu	+ 0.14	+ 0.44
Fe_3O_4/Ag_2SO_4 soln. satd./Ag	- 0.30	+ 0.39

Nernst's equation for various conditions	
conditions	current density cation 1)
charged membranes $c_1 \neq c_2$ passage of current	$i_1^+ = -u^+ \cdot K^+(a_2^+ \zeta - a_1^+)^2$ $K^+ = \frac{RT}{\delta} \cdot \frac{(a_2^+ - a_1^+) - 0.5 \omega \bar{K} \cdot \ln \zeta}{(a_2^+ \zeta - a_1^+)} \cdot \frac{\ln \zeta}{\ln \bar{K}}$ in which $\bar{K} = \frac{a_2^+ + 0.5 (\ln \bar{K} \zeta / \ln \bar{K}) \cdot \omega \bar{K}}{a_1^+ + 0.5 (\ln \bar{K} \zeta / \ln \bar{K}) \cdot \omega \bar{K}}$
charged membranes $c_1 = c_2$ passage of current	$i_1^+ = -u^+ \cdot K^+ \cdot x(a_2^+ \zeta - a_1^+)$ $K^+ = \frac{RT}{\delta} \cdot \frac{2.3 \log \zeta}{(\zeta - 1)}$
neutral membranes $\omega \bar{K} = 0$; $c = a$; $x = 1$ free diffusion	$i_1^+ = -u^+ \cdot K^+ \cdot (c_2^+ \zeta - c_1^+)$ $K^+ = \frac{RT}{\delta} \cdot \frac{c_2 - c_1}{c_2 - c_1} \cdot \frac{\ln (c_2 \zeta / c_1)}{\ln (c_2 / c_1)}$

1) for anions the following substitutions have to be carried out in these equations:
 u^+ by v^+ , a^+ by a^- ; ζ by $1/\zeta$ (except for ζ in the term $0.5 \omega \bar{K} \ln \zeta$) and also $(a_2^+ \zeta - a_1^+)^2$ by $(a_2^- - a_1^-)^2$ $1/x$.

2) $(a^+ \zeta)$ is an expression for the electrochemical activity \bar{a}^+ , in analogy with Guggenheim (95) defined by the electrochemical potential $\mu^+ = \mu^o + R \bar{T} (\ln \bar{a}^+)$; ζ has therefore the meaning of an electrochemical activity coefficient (see also remark in section V.C.3).

3) i.e. the total concentrations on both sides of the membrane are the same.

Bore electrolysis with cellulose membrane using acid and alkali trihalide liquids

Exp. No.	anolyte conc. (mEq/l)	catholyte conc. (mEq/l)	pH begin	pH end	Chl. rate discharge (1/h)	pH begin	pH end	q(20,20)		q(10,10)	
								q(20,20)	q(10,10)	q(20,20)	q(10,10)
1	NaCl	30	0.25	NaCl	8	0.15	3.9	4.1	4.1	6	10.4
	H_2SO_4	10	deas.			deas.					48
2	NaCl	30	0.25	NaCl	8	0.15	4.0	4.2	4.0	6	7.0
	H_2SO_4	20	deas.			deas.					2.6
3	NaCl	30	0.25	NaCl	8	0.15	3.8	3.9	3.8	6	7.0
	H_2SO_4	40	deas.			deas.					2.3
4	NaCl	30	3	NaCl	8	0.15	3.8	4.0	4.0	6	7.0
	H_2SO_4	40	deas.			deas.					7.0
5	NaCl	30 (2)	0.25	NaCl	30	0.15	4.0	3.7	3.9	8	7.0
	H_2SO_4	10	deas.			deas.					11.8
6	NaCl	30 (1)	0.25	NaCl	30	0.15	4.0	5.3	4.5	8	7.0
			deas.			deas.					3
7)	NaCl	30	0.25	NaCl	30	0.15	4.0	4.9	4.3	6	7.0
			deas.			deas.					11.8
8)	NaCl	30	0.25	NaCl	30	0.15	3.9	4.4	4.0	6	7.0
			deas.			deas.					11.3
9	NaCl	30	0.25	NaCl	30	0.15	3.9	4.1	4.0	6	7.0
			deas.			deas.					-
10	NaCl	30	0.5	NaCl	30	0.15	3.7	3.6	3.6	6	7.0
			deas.			deas.					12.3
11)	Cl^-	30	4	$CH_3CO_2^-$	20	0.1	3.4	6.4	5.6	8	7.0
	Zn^+	30	30	Zn^{2+}	10	deas.					10.3
					30	30					48
											30
											36

1) a backfilled anode membrane is used

2) air was passed through the anolyte (rate 50 l/h)

3) nitrogen was passed through the anolyte (rate 6 l/h)

Electrodialysis with treated cellophane membranes using neutral rinsing liquids.

Exp.-No.	Anolyte conc. Ca^{2+}/L	Catholyte conc. Ca^{2+}/L	Voltage (V)	dissolve ^a)		q(30,20)	q(30,10)	Membrane
				begin	end			
12	30	5.0	30	5.0	5.2	7.0	12	-
13	30	4.0	30	4.0	5.6	7.0	24	-
14	30	5.5	30	8.0	10	8.4	24	-
15	30	4.0	30	4.0	12	15	24	-
16	30	5.0	30	6.0	5.0	5.1	7.0	-
17	29	4.0	29	4.0	7.6	8.0	7.6	24
18	29	4.0	29	4.0	12	8.2	8.1	36
19	30	5.0	30	5.0	8.8	5.7	6.2	7.0

^a *in* vitro. rate 6 1/h.

2) membrane treated with a 20% solution of bakelite.

The charge efficiency of the chloride ion for different slightly-selective membranes

Exp. no.	membrane ¹⁾	cathode ²⁾	anode ³⁾	chlorate ⁴⁾		chlorate ⁵⁾		chlorate ⁶⁾		membrane	
				composition rate (1/h)	rate (1/h)	$\phi_{Cl^-}(1/2)$ (eq $Cl^-/1$)	$\phi_{Cl^-}(1/2)$ (eq $Cl^-/1$)	$\phi_{Cl^-}(10)$ bedside and anode	$\phi_{Cl^-}(10)$ anode cathode	$\phi_{Cl^-}(10)$ cathode	$\phi_{Cl^-}(10)$ cathode
20	30 Cl^- 20 Br^- 10 As^-	0.15 dose	31 Cl^- 0.15 dose	0.15 dose	30	18	7.0	3.0	18	—	—
21	30 Cl^- 20 Br^- 10 As^-	0.15 dose	31 Cl^- 0.15 dose	0.15 dose	30	11	7.0	4.2	30	24	P-lacquer
11	30 Cl^- 20 Br^- 10 As^-	4 cath.	10 Cl^- 20 Br^- 30 As^-	0.1 cath.	30	6	7.0	10.3	48	30	halide lacquer (10)
22)	30 $NaCl$	4 dose	30 Cl^- 1.0 ⁴⁾	31	14	7.0	8.8	27	—	—	halide lacquer (10)

¹⁾ normal staining method²⁾ cath. rate 6 1/h³⁾ staining with the use of a diazo⁴⁾ the cathode was neutralised by 3.10 n $NaCl$.

Some physico-chemical data on a couple of selective membranes described in this report.

membrane	polarity	exchange ¹ cap. (meq./g.)	resistance of 1 cm ² membrane in 0.1 n KCl (Ω)	thickness (mm)	0.1/n	0.01/n	diffusion potential (mv) 0.001/n
Permionic CR 51	-	0.71 ²)	38	0.9	48	50	-
" ARX 44	+	-	270	0.55	48	-	-
" ARX 102	+	0.36	17	0.50	45	47	-
T.K.O. A 19	+	0.15	38	0.13	29.5	48.5	49.5
T.K.O. A 40	+	0.36	8	0.20	24	42	48
T.K.O. A 17b	-	0.15	46	0.13	18.4	44.8	48.0

1) the number meq. HCl or NaOH required for the neutralisation of 1 g membrane.

2) the exchange cap. of membrane ARX 44 could not be determined as it partly dissolved on treating with diluted caustic.

A.T.A-T.N.O.
T.A. No 270
Table XII.

Influence of current density on $q(c_p, c_k)$ with the use
of membrane combination ARX 102 - CR 51¹⁾

exp. no	current density (ma/cm ²)	$q(30-20)$	$q(20-10)$	$q(30-10)$
23	1.9	17	9	16
24	3.1	16	11	13
25	5.8	8	5	6
26	10.0	5	5	5

¹⁾ cell A2; middle compartment 6 mm wide;
circ. rate dialysate 8-10 1/h.

A.T.A.-T.N.O.
T.A. No 270.
Table XIII.

Influence on q of current density and stirring of the dialysate
with the use of different combinations of membranes ¹⁾

exp no	current density (ma/cm ²)	q g NaCl/ 100 amp.hr	dialysate		anodic membrane
			circ.	stirring	
27	1.9	174	-	-	A 19
28	2.4	168	-	-	A 19
29	2.8	150	-	-	A 19
30	3.3	90	-	-	A 19
31	6.5	132	-	-	A 19
32	10.8	132	-	-	A 19
33	40	126	²⁾	-	A 19
34	2.7	192	-	+	A 19
35	6.5	180	-	+	A 19
36	10.0	150	-	+	A 19
37	1.9	156	-	-	ARX 44
38	10.8	102	-	-	ARX 44
39	2.7	210	-	+	ARX 102
40	6.5	186	-	+	ARX 102
41	10.8	132	-	+	ARX 102
42	10.8	54	-	-	ARX 102

¹⁾ cell A 1; middle compartment 31 mm wide;
cathodic membrane CR 51²⁾ in this experiment the middle compartment was 11 mm wide.

Preliminary determinations of the magnitude of diffusion
with the use of some selective membranes¹

exp. no.	time (h)	membranes ²		conc. rinising compartment (meq.Ol ⁻¹ /l)	increase conc. dialysate compartment (meq.Ol ⁻¹ /l)	
		anodic	cathodic		after T h.	per 100 h
43	5	A 19	membrane filter (coarse)	31	15	300
44	5	A 19	membrane filter(fine)	31	14	280
45	2	cell.(Visk.)	cell.(Visk.)	24	5	250
46	16	cell.(Visk.)	cell.(Visk.)	24	17	110
47	17 ¹	A 19	CR 51	31	2	10
48	48	A 19	CR 51	31	5	10

1) cells A₁ and A₂
2) membrane area 37 cm²

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T.A.No 270
Table XV.

Influence of chloride concentration and pH of the anolyte on the removal of chlorine at the anode in a two-compartment cell with non-reversible electrodes

Exp. no.	anolyte ¹⁾			q(c _p) (g NaCl/100 amp.hr)
	chloride content meq/l	active chlorine content (end) meq/l	pH aver.	
52 ²⁾	30	6	15	80
53	30	5	7.0	50
54 ³⁾	30	0.4	1.1	90
55 ²⁾	20	5	1.7	60
56	20	5	5.1	40
57	20	4	7.0	40
58 ²⁾	10	4	1.9	40
59	10	3	4.2	30
60	10	4	7.4	30

¹⁾ a diluted solution of sodium chloride (circa. rate 6 l/h);
dos. rate catholyte (NaOH: 20 meq/l) 0.15 l/h.

²⁾ Anolyte: a diluted hydrochloric acid solution.

³⁾ outside the cell air was passed through the anolyte
(rate 100 l/h) to decrease its active chlorine content.

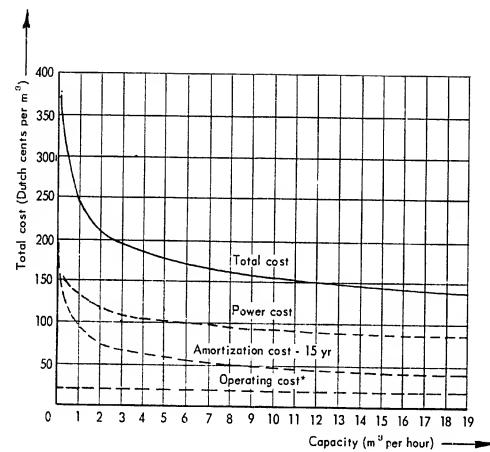
Data concerning some desalting experiments of potassium chloride solutions with reversible silver-silver chloride-electrode

Exp. no.	Anolyte		Catholyte		duration electrolysis (min.)	over-voltage electrolysis (voltage) (v)	over-energy consumption (amp. hr.)	$\frac{S(\text{O}_2\%)}{(\text{amp.}^2/\text{hr.}^2)}$	$\frac{S(\text{O}_2\%)}{(\text{amp.}^2/\text{hr.}^2)}$
	$\frac{\text{O}_2}{\text{KCl}}$ (l.)	$\frac{\text{O}_2}{\text{KCl}}$ (l.)	$\frac{\text{O}_2}{\text{KCl}}$ (l.)	$\frac{\text{O}_2}{\text{KCl}}$ (l.)					
61	0.39	27	24	0.39	27	0.9	0.48	0.05	1.0
62	0.40	14	8	0.39	28	12	0.65	0.05	72
63	0.50	19	14	0.50	28	72	0.48	0.02	54
64	0.50	19	6	0.50	28	72	0.73	0.04	76
65	0.50	27	17	0.50	27	72	0.73	0.06	90
						1 x 33	0.71		102
						1 x 30	0.66		66
						1 x 21.5	0.6		

¹ maximal value is $\frac{75.5}{30.5} \times 100\% = \frac{75.5}{30.5} \times 200.4 = 202 \text{ g KCl}/100 \text{ amp. hr.}$

² for comparing with the O_2 -value of section VI.B, C and D.

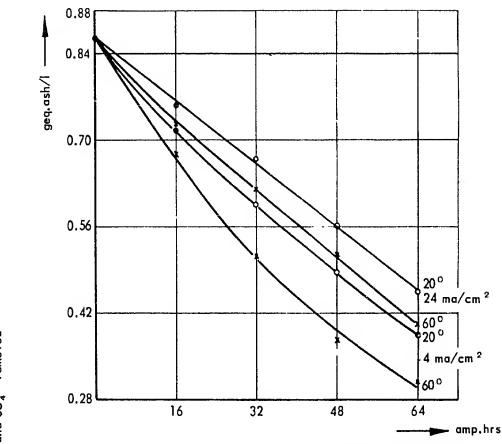
³ frequency of reversing polarity was increased to prevent fading of the voltage.



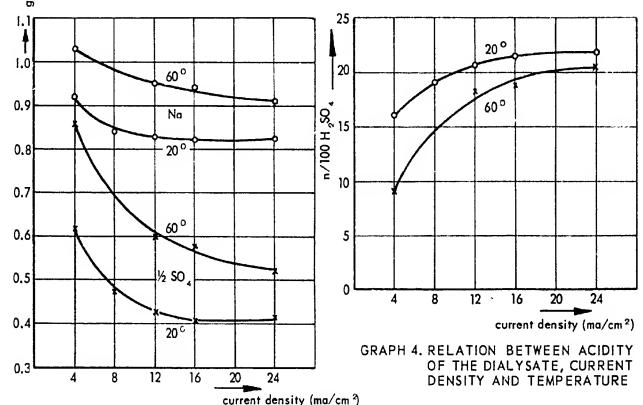
*Labour, maintenance, supplies, etc.

EFFECT OF CAPACITY ON OPERATING COSTS

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TA-no 270
GRAPH 1



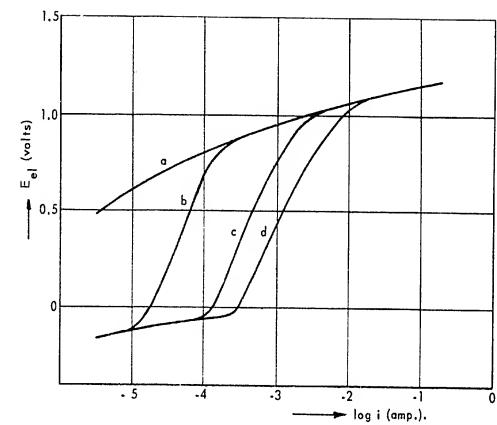
GRAPH 2. THE COURSE OF THE SODIUM SULPHATE REMOVAL AGAINST THE NUMBER OF AMP. HRS AT DIFFERENT TEMPERATURES



GRAPH 3. RELATION BETWEEN REMOVAL OF SODIUM AND SULPHATE IONS, CURRENT DENSITY AND TEMPERATURE

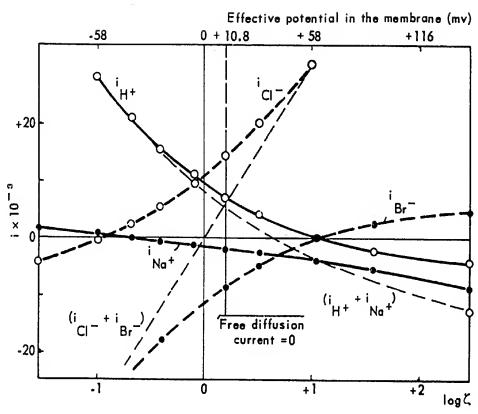
THE EXPERIMENTS OF HOFFMAN

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T.A.-no 270
GRAPHS 2,3 & 4



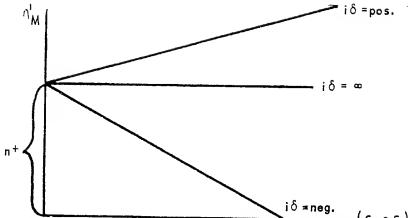
a. in nitrogen atmosphere
b. in contact with air
c. air passed through (low rate)
d. air passed through (high rate)

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TA-no 270
GRAPH 5

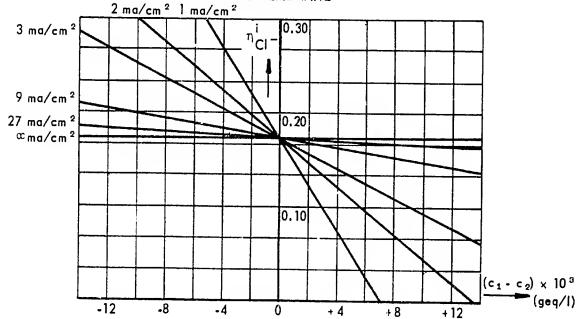


DIAGRAMMATIC EVALUATION OF THE EQUATION OF TEORELL FOR
THE INDIVIDUAL CURRENT DENSITIES CONNECTED WITH THE VARIOUS
ION SPECIES AT PASSAGE OF CURRENT AND EQUAL TOTAL
CONCENTRATIONS IN A SPECIFIC CASE

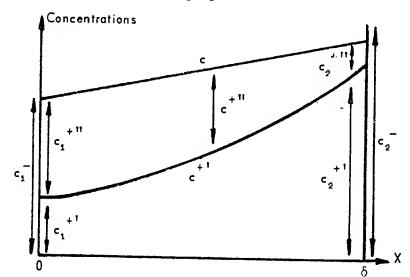
A.T.A.-T.N.O.
TA-ne 270
GRAPH 6



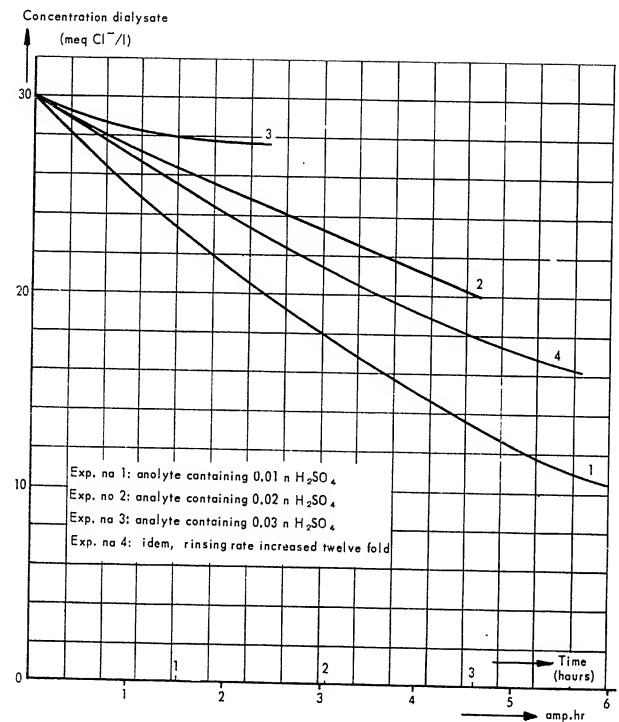
GRAPH 7. CURRENT DENSITY EFFICIENCY OF THE CATION IN A TWO-ION SYSTEM AS A FUNCTION OF CONCENTRATION DIFFERENCE ($c_2 - c_1$) ON EITHER SIDE OF THE MEMBRANE

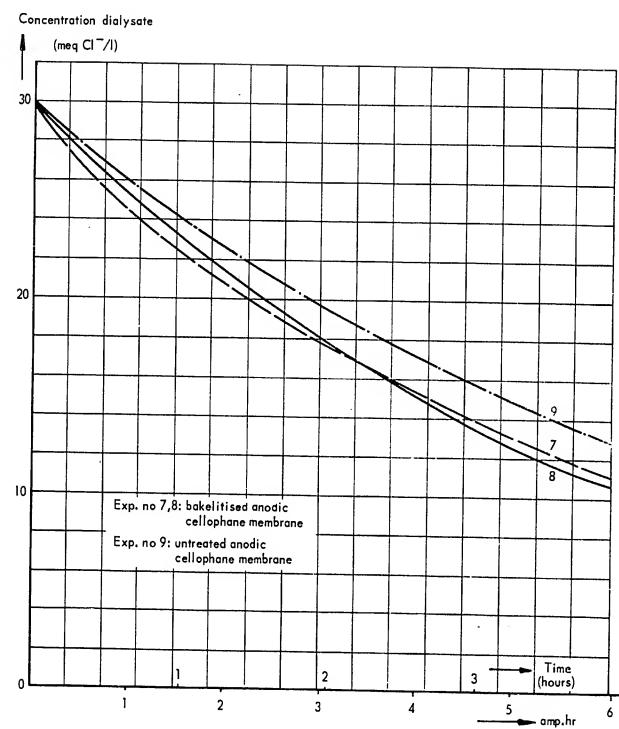


GRAPH 8. CURRENT DENSITY EFFICIENCY OF THE CHLORIDE ION IN A TWO-ION SYSTEM (HCl) AS A FUNCTION OF THE CONCENTRATION DIFFERENCE ($c_1 - c_2$)



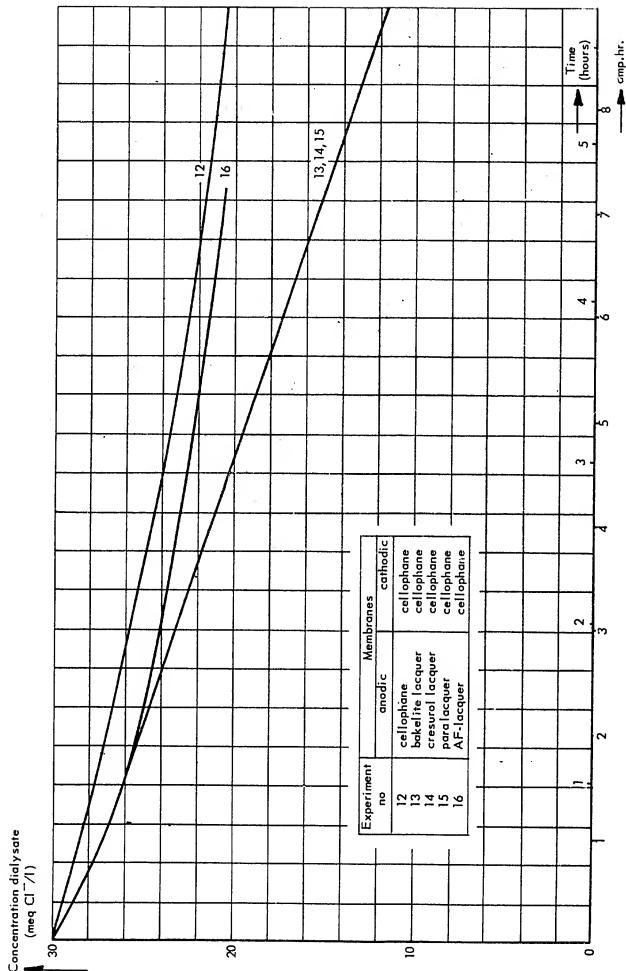
GRAPH 9. SCHEMATIC DRAWING OF THE CONCENTRATIONS OF THE IONS IN A THREE-ION-SYSTEM





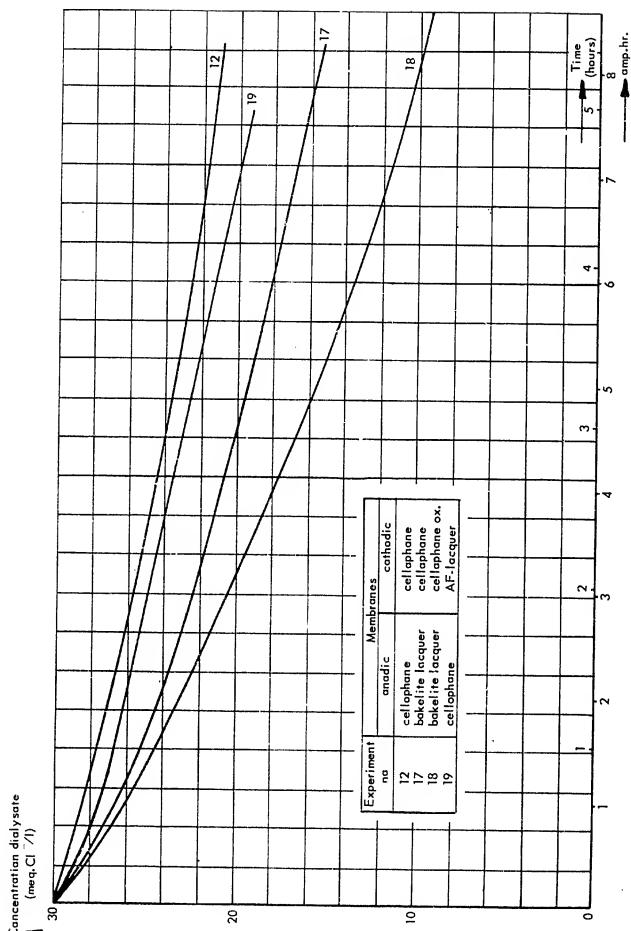
DESALTING CURVES OBTAINED IN EXPERIMENTS WITH BAKELITISED AND NON-TREATED ANODIC CELLOPHANE MEMBRANES (CONDITIONS OF TABLE IX)

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TA-no 270
GRAPH. 11



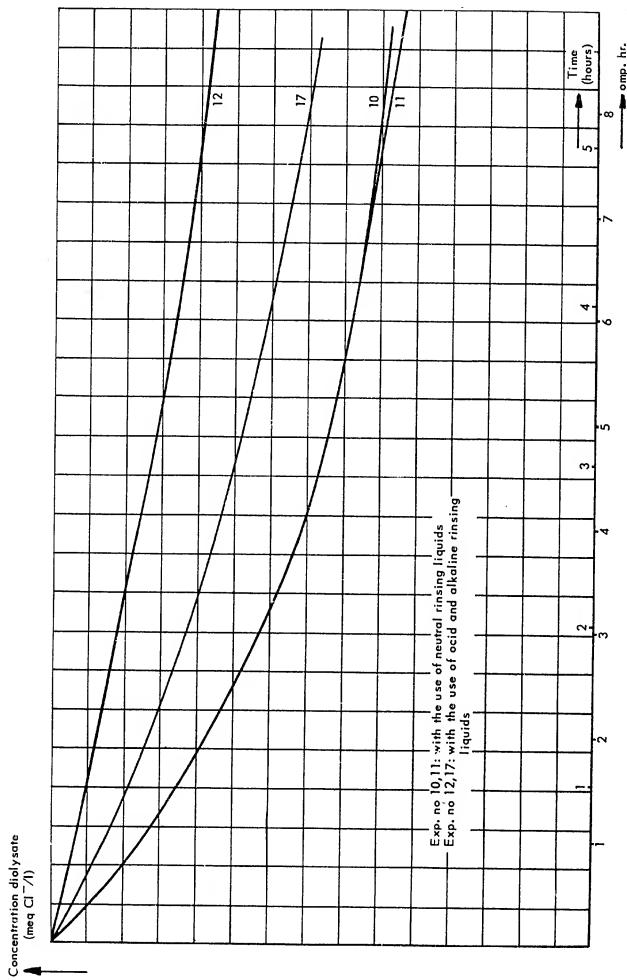
DESMALTING CURVES OBTAINED IN EXPERIMENTS WITH ANODIC CELLOPHANE MEMBRANES TREATED IN VARIOUS WAYS (CONDITIONS CF TABLE X)

A.T.A.-T.N.O.
TA-no 270
GRAPH 12

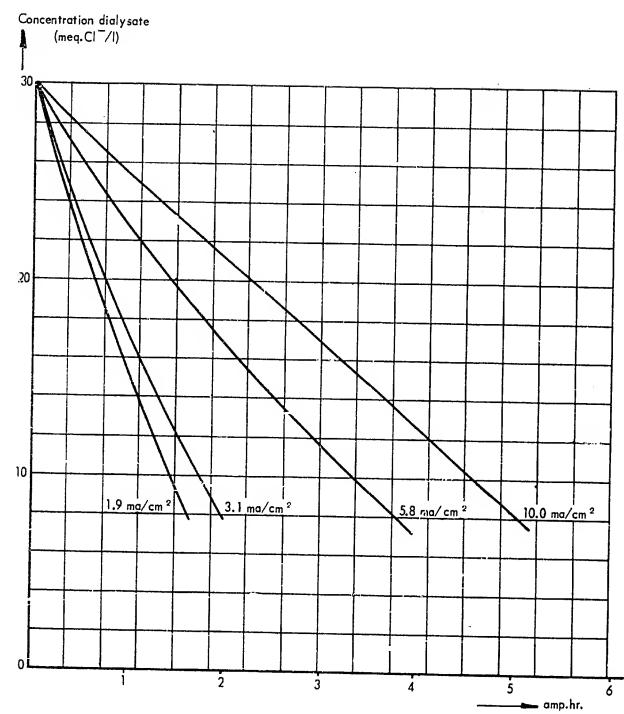


DEASALTING CURVES OBTAINED IN EXPERIMENTS WITH CATHODIC CELLOPHANE MEMBRANES TREATED IN VARIOUS WAYS (CONDITIONS CF TABLE X)

A.T.A.-T.N.O.
TA-no 270
GRAPH 13

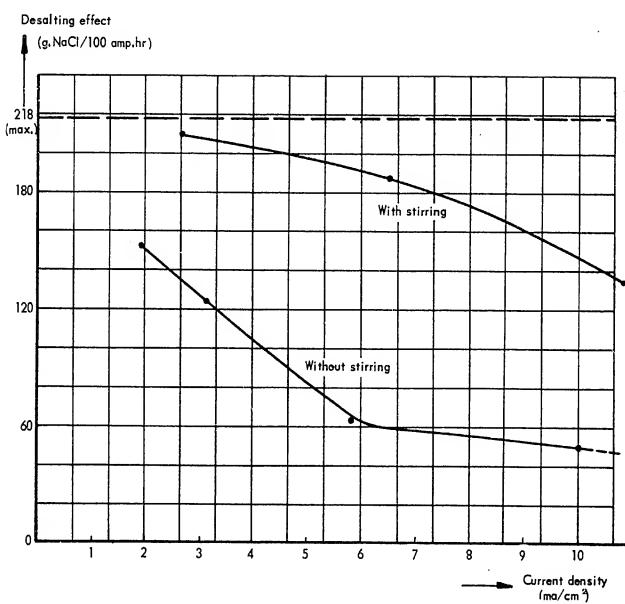


RETARDATION OF DESALTING WITH NON- AND SLIGHTLY PERMEABLE MEMBRANES BY USING NEUTRAL RINSING LIQUIDS (CONDITIONS
OF TABLES IX AND X)



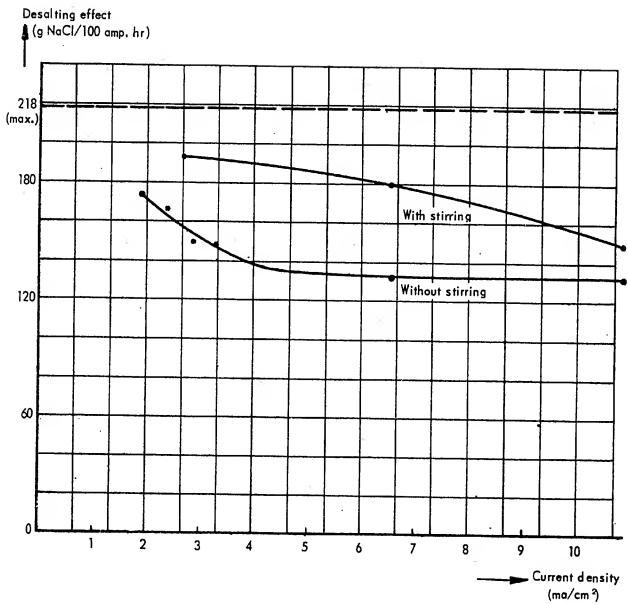
RELATION BETWEEN CHLORIDE CONCENTRATION OF THE DIALYSATE AND THE NUMBER OF AMP.HR. AT DIFFERENT CURRENT DENSITIES (CELL: A₅; MEMBRANES: ARX 102 - CR 51)

A.T.A.-T.N.O.
TA-no 270
GRAPH 15



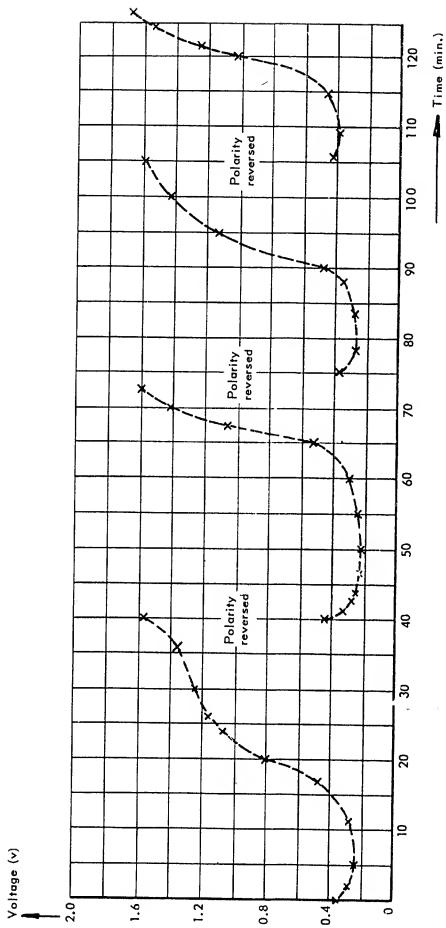
RELATION BETWEEN THE DESALTING EFFECT AND CURRENT
DENSITY WITH AND WITHOUT STIRRING OF THE DIALYSATE (CELL
A2; MEMBRANES: ARX 102 - CR 51)

A.T.A.-T.N.O.
TA-no 270
GRAPH 16



RELATION BETWEEN THE DESALTING EFFECT AND CURRENT
DENSITY WITH AND WITHOUT STIRRING OF THE DIALYSATE (CELL
A2; MEMBRANES: A 19 - CR 51)

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TA-no 270
GRAPH 17



RELATION BETWEEN VOLTAGE AND TIME AT THE ELECTROLYSIS IN A TWO-COMPARTMENT CELL EQUIPPED WITH SILVER-SILVERCHLORIDE ELECTRODES (EXP. 64)

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T.A.-no 270
GRAPH 18

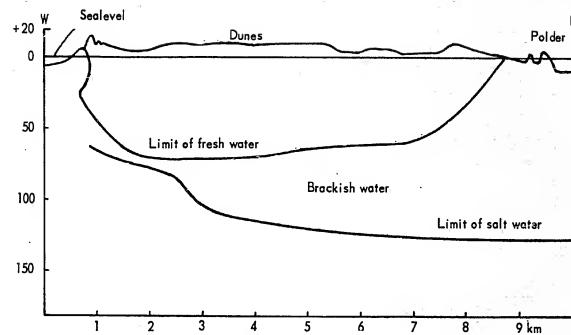


FIG. 1 CROSS-SECTION OF THE DUNES SOUTH OF HAARLEM

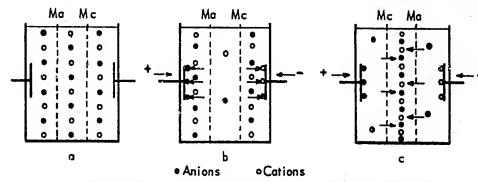


FIG. 2 DIAGRAMMATIC REPRESENTATION OF ELECTRODIALYSIS IN A THREE COMPARTMENT CELL WITH THE USE OF SELECTIVE MEMBRANES

a at the beginning of the process

b after electrodialysing with the anode adjacent to the anion-permeable membrane

c after electrodialysing with the anode adjacent to the cation-permeable membrane

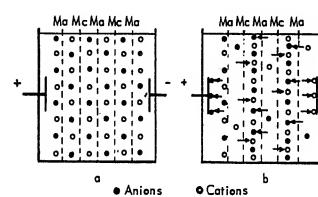
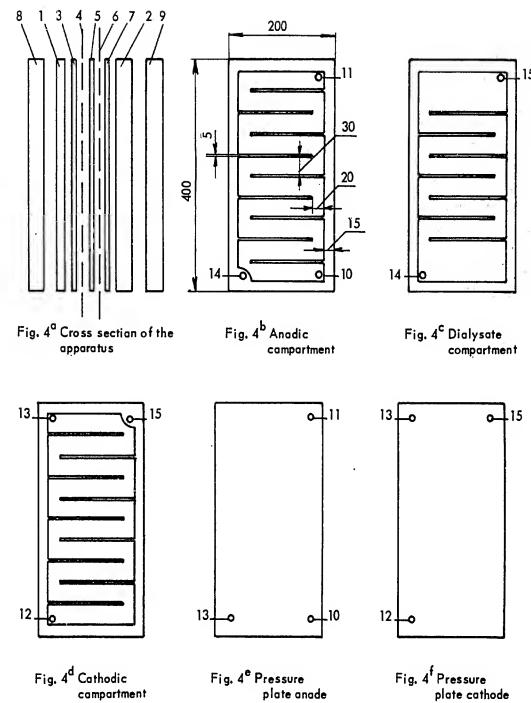
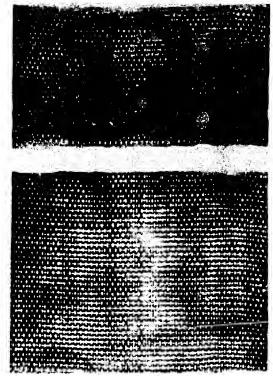


FIG. 3 DIAGRAMMATIC REPRESENTATION OF AN ELECTRODIALYTIC CELL WITH A NUMBER OF SELECTIVE MEMBRANES



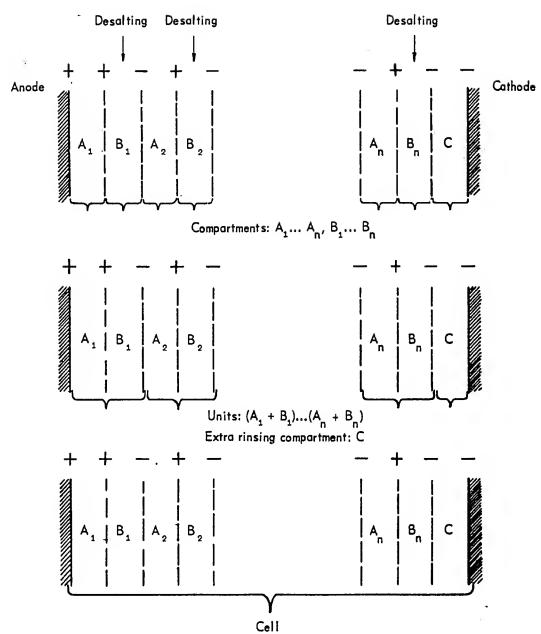
1 Anode	7 Cathodic compartment	12 Catholyte supply
2 Cathode	8 Pressure plate anode	13 Catholyte outlet
3 Anodic compartment	9 Pressure plate cathode	14 Dialysate supply
4,6 Membranes	10 Anolyte supply	15 Dialysate outlet
5 Middle compartment	11 Anolyte outlet	

Approved For Release 2002/08/28 : CIA-RDP82-00041R000100160001-0



PICTURE OF CORRODED MEMBRANE, DYED WITH TURNBULL'S
BLUE.

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TA-no 270
FIG. 5



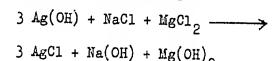
SUBDIVISION OF A CELL INTO UNITS AND COMPARTMENTS

A.T.A.-T.N.O.
TA-na 270
FIG. 6

Summary of patents in the United States, Great Britain, Germany, France, Switzerland and the Netherlands, concerning various processes for the purification of water for industrial use and of drinking water, distillation processes excepted (up to 1951).

U.S. Pat. 2,322,689
= British Pat. 570,670
22-6-1943 (4-8-1942)
A. Goetz, Pasadena;
Sunshine Mining Comp.

Chemical process for production of potable water from non potable saline water.
Mainly NaCl and MgCl₂ must be removed from seawater. For the removal of NaCl silversalts are used such as silver-carbonate and silveroxide. A colloidal suspension of silver oxide in fresh water is prepared and this is added to the seawater.



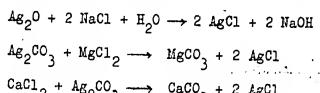
Almost all the silverchloride precipitates. The magnesium hydroxide formed is practically insoluble in water and both substances can be removed by filtration. The sodium hydroxide formed can be removed by a weak organic acid, e.g. by citric acid.

Barium hydroxide is added in order to remove the MgSO₄, present in the seawater. Both the barium sulphate and the magnesium hydroxide formed a precipitate.

U.S. Pat. 2,363,020
21-11-1944 (8-6-1943)
Cl. R. Spearman.

Method for chemical demineralization of sea water.

The treatment of sea water with silver oxide or silver carbonate and subsequently with uric acid, e.g.:



The sodium-ions are removed by uric acid under the formation of an insoluble

A.T.A.-T.N.O.
T.A. No 270.
Appendix 1.

sodium ureate. Other cations are also partly or completely removed as insoluble ureates.

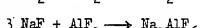
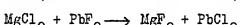
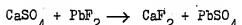
U.S. Pat. 2,373,884

17-4-1945

Prior Gr. Britain: 16-6-1943
= British Pat. 567,529
H.R. Frisch, Caterham-on-the-Hill.

Production of fresh water from salt water.

Seawater is treated with a mixture of lead fluoride and aluminium fluoride or iron fluoride (molar ratio 3:1). I.a. the following reactions take place:



If seawater contains 36 g of salts/l, the salt content falls after 1 hour to 9 g/l, after 8 hours to 3 g/l and after 24 hours to 0.5 g/l. The lead fluoride used may be used again to reduce the salt content of fresh seawater from 36 g/l to 30 g/l. 3% of seawater are added in order to remove traces of lead and fluoride from the desalinated water.

U.S. Pat. 2,374,116

17-4-1945 (25-3-1944)
H.D. Meincke Jr.
H.D. Meincke Sr.
Gleucos

Treatment of water containing chlorides dissolved therein.

The mixing of seawater with phenyl mercury gluconate or phenyl mercury glutaminate (135 g to 560 cc of water). This mixture is stirred for 5 minutes. 86% 92% of the sodium chloride present is precipitated in the form of the insoluble phenyl mercury chloride. In order to reduce the pH of the water, a quantity of uric acid is added (1 mg per 100 cc of water).

U.S. Pat. 2,445,669
20-7-1948 (22-6-1943)
A. Goetz, Pasadena;
Sunshine Mining Co.

Chemical process for production of potable water from nonpotable saline water.

Modification of U.S. Patent Spec. No. 2,322,639: silveroxide-bariumhydroxide zeolites are added to the mixture.

A.T.A.-T.N.O.
T.A. No 270.
Appendix 1.

British Pat. 582,710
(26-11-1946 (4-3-1944)
(13-3-1943)
Ocean Salts (Products)
Ltd. London;
B.A. Adams, Barry;
Th.H.E.Kressman, London.

French Pat. 630,533
(5-12-1927 (8-3-1927)
M.M.G. Malcor, France.

Swiss Pat. 227,970
(31-7-1943)
Prior Germany: 1-2-1939
L. Seibold, Vienna.

Dutch Pat. 13,435
= Ger. Pat. 383,666
= Fr. Pat. 557,861
= Br. Pat. 211,562
17-6-1925 (16-2-1925)
Elektro-Osmose A.G.
(Graf Schwerin Gesellschaft)
Berlin.

Obtaining drinking water from sea- and other saline-waters.

The treatment of sea water with a silver-compound (Ag_2O , Ag_2CO_3 , Ag_2SO_4) mixed with an earth alkali oxide or hydroxide, e.g. of Ba and Ca. After the filtration the filtrate is treated with an ion-exchanger or with uric acid if desired.

Procédé d'utilisation de l'eau de mer en vue de l'obtention séparée d'eau douce et des sels dissous.

The water is frozen. The formed ice is removed and melted.

Gerät zum Ausscheiden von gelösten Stoffen aus Lösungen auf elektro-osmotischen Wege.

Apparatus for the electro-osmotic separation of dissolved substances, consisting of at least one electro-osmotic cell, the anode-surface of which amounts to at most 1/100 of the outer surface of the anode diaphragm. The distance between anode- and cathode-diaphragm is from 10-20 mm and the distance between cathode and cathodediaphragm is at least of the same order.

Werkwijze voor het ontharden en ontzouten van water.

A thin layer of the water to be desalinated is exposed in a three compartment-cell to the action of direct current with the application of diaphragms. These diaphragms permit the passage of anions and cations, but prevent the water-diffusion from the middle-compartment to the cathode- and anode-compartments. A distance of 2 cm from the diaphragms has been ascertained to be the greatest and most practical thickness of said layer.

A.T.A.-T.N.O.
T.A.No. 270.
Appendix 1.

U.S. Pat. 2,522,856
19-9-1950.

Removal of salt from seawater.

Seawater is made potable by addition of Ag_2SiF_6 and $\text{Ca}(\text{OH})_2$. The process is carried out by first adding the Ag_2SiF_6 to sea water. After the solids are settled, the H_2O is decanted and filtered and CaO is added to the filtrate. When the reaction is completed the solids are allowed to settle, and the supernatant H_2O is ready for drinking. One gallon of sea water requires 348 g Ag_2SiF_6 and 12,3 g CaO .

U.S. Pat. 2,546,071
20-3-1951
Wm. A.E. Hult.

Apparatus for obtaining fresh water from sea water.

The apparatus provides for treatment of sea water with commercial AgNO_3 in an agitator and passage of the treated water through a "rifle barrel" sluice pipe to recover the resultant precipitate of AgCl . A settling tank receives the treated water from which more AgCl is precipitated. The water is then led into evaporating ponds for extraction of commercial nitrates or for use as irrigation water. Precipitation is greatly aided by the ridges and corrugation of the sluice pipe.

British Pat. 454,993
= French Pat. 797,984
12-10-1936 (1-2-1936)
Pr. F. Steingiesser,
Bad Salzuflen.

Improvements in the production of drinking water from sea water.

Sea water is partly frozen. The ice is removed and melted.

✓ British Pat. 568,129
20-3-1945 (10-4-1943)
(13-3-1944)
Ocean Salts (Products)
Ltd. London.
B.A. Adams, Barry;
H.R. Bott, Slough.

Obtaining drinking water from sea and other saline waters.

The treatment of sea water with a copper-compound, e.g. copper sulphate and subsequently with a reducing agent, e.g. barium oxide, or with a cation-exchanger.

A.T.A.-T.N.O.
T.A. No 270.
Appendix 1.

Dutch Pat. 51,142.
= Br. Pat. 507,597
= Fr. Pat. 830,599
16-9-1941
Prior Belgium: 19-12-1936
J.W.A. Convert, Brussel;
P.P.J.F. Mommen, "

Inrichting voor het electrolytisch ont-trekken of concentreren van in een vloeistof opgeloste of gesuspendeerde stoffen aan (in) een oplossing of een mengsel.

The apparatus consists of a number of compartments provided with electrodes, said compartments consisting of tubes having an impermeable cylindrically, resp. prismatically shaped wall, the basis of which and/or the immediate vicinity thereof has been executed as a filter. If the apparatus is used, the filter remains under the level of the liquid and means have been applied for the withdrawal of liquid from the inside of the electrode-tubes in order to obtain a hydrostatical fall of pressure in the filter-walls, said fall of pressure taking place in the direction of the electrodes.

A.T.A.-T.N.O.
T.A. No 270.
Appendix 1.

Summary of the numbers of patents relating to desalting
of water by means of distillation (up to 1950)

<u>U.S.Pat.</u>	<u>U.S.Pat.</u>	<u>British Pat.</u>	<u>French Pat.</u>
2,475,482	2,027,395	2,813 AD 1912	925,865
2,475,481	1,577,675	13,121 AD 1910	921,418
2,456,562	1,477,328	11,421 AD 1909	911,617
2,455,835	1,440,723		899,141
2,455,834	1,396,316		883,251
2,445,350	1,361,910		877,456
2,445,907	1,359,276	744,366	854,336
2,424,142	1,355,935	738,602	823,765
2,420,935	1,354,122	627,798	756,061
2,420,819	1,353,521	606,180	686,847
2,413,101		574,995	541,380
2,412,466		570,222	536,888
2,405,877	In 85 b 2	523,087	500,255
2,405,118	U.S.Pat.	494,408	453,442
2,402,737	2,456,524	457,165	444,949
2,398,842		385,293	444,948
2,398,836		382,076	443,914
2,398,292	British Pat.	381,904	420,613
2,398,291	605,728	371,969	356,762
2,398,068	600,784	371,195	346,425
2,392,255	582,589	362,225	344,363
2,384,226	579,514	319,103	
2,383,294	577,162	303,710	
2,383,234	572,333	299,311	
2,378,350	567,103	293,201	54,485
2,376,876	564,634	271,465	51,186
2,376,146	555,227	262,363	47,786
2,375,640	538,999	199,341	41,033
2,374,519	531,970	182,555	26,992
2,368,588	528,145	179,392	21,753
2,366,189	485,075	172,596	11,281
2,358,559	362,729	169,227	238
2,357,869	289,120	166,518	
2,342,201	189,879	142,145	
2,342,062	139,746	134,523	
2,332,294	121,418	82,082	
2,324,663	112,679	64,471	
2,320,853	112,223	53,397	
2,305,408	111,480	47,446	
2,254,538	28,537 AD 1913	47,219	
2,199,320	14,766 AD 1913		
2,141,330	5,016 AD 1913		
2,079,897	1,704 AD 1913		
2,078,377	11,553 AD 1912		
		945,581	

A.T.A.-T.N.O.
T.A. N° 270.
Appendix 2.

Summary of patents in class 12 h 5
(electro-osmosis) up to 1950

U.S. Pat. 1,840,105

Liquid purification.
5-1-1932 (15-3-1928)
R.H. Kean,
General Zeolite Comp., Chicago.

U.S. Pat. 1,860,676

Liquid purification.
31-5-1932 (25-10-1928)
R.H. Kean,
General Zeolite Comp., Chicago.

U.S. Pat. 1,861,796

Liquid treatment.
7-6-1932 (6-9-1928)
A.B. Hodges,
General Zeolite Comp., Chicago.

U.S. Pat. 1,864,767

Purification apparatus.
28-6-1932 (19-3-1928)
H.J. Schneiderwirth, New York.

U.S. Pat. 1,878,237

Electrical purification of water.
20-9-1932 (24-4-1930)
W.F. Hoffman a.o.,
Northwest Paper Comp.

U.S. Pat. 1,901,652

Liquid purification.
14-3-1933 (25-8-1928)
R.H. Kean,
General Zeolite Comp., Chicago.

British Pat. 352,109

Improvements in or relating to
the electrolytic purification
of aqueous solutions.
9-7-1931
Prior Germany 12-4-1929
Dr J. Billiter, Vienna.

British Pat. 431,695

Improvements in electrical
purification of liquids.
15-7-1935 (13-1-1934)
J. Billiter, Paris.

German Pat. 394,360

8-3-1922
Add. to Ger. pat. 383,666
Elektro-Osmose A.G.
(Graf Schwerin Gesellschaft), Berlin.

Verfahren zur vollständigen oder teilweisen Beseitigung von Salzen aus Wasser auf elektro-osmotischen Wege.

German Pat. 395,752

8-3-1922
Add. to Ger. pat. 383,666
Elektro-Osmose A.G.
(Graf Schwerin Gesellschaft), Berlin.

Verfahren zur vollständigen oder teilweisen Beseitigung von Salzen aus Wasser auf elektro-osmotischen Wege.

German Pat. 498,048

17-5-1930 (27-6-1928)
Siemens Elektro-Osmose G.m.b.H.,
Berlin.

Verfahren zur elektro-osmotischen Reinigung von Flüssigkeiten.

German Pat. 579,023

20-6-1933 (23-8-1930)
Siemens Elektro-Osmose G.m.b.H.,
Berlin.

Einrichtung zur elektrodialytischen Reinigung von Flüssigkeiten.

German Pat. 533,846

19-9-1931 (18-5-1929)
Siemens & Halske A.G., Berlin

Verfahren zur Durchführung elektro-osmotischer Reinigungen von Flüssigkeiten.

German Pat. 531,155

6-8-1931 (30-5-1929)
Add. to pat. 498,048
Siemens Elektro-Osmose G.m.b.H.,
Berlin.

Verfahren zur elektro-osmotischen Reinigung von Flüssigkeiten.

French Pat. 696,871

20-10-1930
Prior Germany 15-6-1929
Kali-Chemie A.G., Germany.

Procédé d'épuration de solutions d'eau oxygénée.

Swiss Pat. 100,202

16-7-1923
Prior Germany 10-9-1921
Elektro-Osmose A.G., Berlin.

Verfahren zur Beseitigung von Salzen aus Wasser auf elektro-osmotischem Wege.

Swiss Pat. 249,631

15-7-1947
Prior Germany 21-6-1943
L. Seibold, Vienna.

Verfahren zur Reinhal tung einer Flüssigkeit, die der Verunreinigung durch Elektrolyte ausgesetzt ist.

A.T.A.-T.N.O.
T.A.No 270.
Appendix 3.

Summary of patents in class 12 h 3 (diaphragms for electrolytic purposes in general) up to 1950

British Pat. 305,022

10-4-1930
Prior Germany 28-1-1928
Siemens & Halske A.G., Berlin.

A process for the manufacture of porous bodies, more particularly of diaphragms for electro-osmotic purposes.

British Pat. 361,965

Acc. 30-11-1931
Prior U.S.A. 16-9-1929
The Anode Rubber Comp.
Ltd. St. Peter's Port,
Guernsey, Channel-Islands.

Improvements in or relating to diaphragms permeable to the electric current.

German Pat. 73,688

Publ. 2-3-1894
Farbwerke vorm.
Meister Lucius & Brüning, Höchst.

Elektrolytisches Diaphragma.

German Pat. 271,001

Fr. Pat. 471,680, 14-4-1913
Gesellschaft für Elektro-Osmose
m.b.H. Frankfurt.

Diaphragma für elektrochemische oder elektro-osmotische Verwendung.

German Pat. 342,621

Publ. 21-10-1921
E. de Haen, Chemische Fabrik "List"
G.m.b.H., Seelze near Hannover.

Diaphragmen zur Elektrolyse wässriger Lösungen.

German Pat. 576,280

21-6-1930
Siemens & Halske A.G., Berlin.

Herstellung von Diaphragmen.

A.T.A.-T.N.O.
T.A. No 270.
Appendix 4.

Summary of patents in the classes 12 d 1 d (clarifying and separating liquids by electrical action) and 12 h 1 (electrolytic processes and equipment in general) up to 1950

U.S. Pat. 1,371,698
18-7-1921
O. Linder.
Western Electric Comp., New York.

Process and apparatus for completely eliminating salts and other ionized chemicals from their aqueous solution by means of electrolysis.

U.S. Pat. 1,918,477
18-7-1933
Prior Germany 28-6-1929
I.G. Farbenindustrie A.G.
Frankfurt a. Main. H.Lang, Halle.

Purification of electrolytes.

U.S. Pat. 1,996,799
9-4-1935
Prior England: 20-10-1933
D. Johnson Evans, Tonbridge.

Electrolytic cell.

U.S. Pat. 2,093,770
21-9-1937
Prior Germany 15-1-1932
J. Billiter, Vienna.

Electrical purification of liquids.

British Pat. 251,136
= Fr. Pat. 601,031
29-4-1926 (17-6-1925)
M.D. Avery. Chicago.

Improvements in a method of and apparatus for purifying liquids.

British Pat. 601,576
British Pat. 601,578
British Pat. 601,579
British Pat. 601,580
7-5-1948. Prior U.S.A.: 5-6-1945
Dubilier Condenser Comp.Ltd.London.

Improvements in or relating to apparatus for the electrical treatment of fluids.

British Pat. 611,819
4-11-1948. Prior U.S.A.: 12-2-1946
Dubilier Condenser Comp.Ltd.London.
Rectification:
Brit. Pat. 601,579

Improvements in or relating to apparatus for electrically treating fluids.

A.T.A.-T.N.O.
T.A. No 270.
Appendix 5.

German Pat. 45,112

6-2-1888

O.H. Jewell, Chicago.

German Pat. 397,684

12-5-1922

Siemens & Halske, A.G., Berlin.

German Pat. 548,366

22-8-1930

Prior Austria 18-12-1930

= Fr. Pat. 721,507

= British Pat. 368,556

Oestereichische Chemische Werke
Gesellschaft m.b.H., Vienna.

German. Pat. 647,289

6-2-1925

H. Bechhold, Frankfurt a.Main.

French Pat. 329,148

Publ. 25-7-1903. Appl. 6-2-1903

Ch. Mac. Cornick Chapman, U.S.A.

French Pat. 412,634

Publ. 18-7-1910. Appl. 10-1-1910.

Valérie Verfaillie, Belgium.

French Pat. 689,674

10-9-1930 (10-2-1930)

Filtres Philippe S.A.

Austrian Pat. 119,209

10-10-1930 (17-10-1928)

J. Billiter, Vienna.

Austrian Pat. 143,038

J. Billiter, Paris.

Filtrierapparat zur Reinigung von
Flüssigkeiten auf elektrolytischen
Wege.

Filterpressenartiger Apparat für
elektrolytische und elektro-osmo-
tische Zwecke.

Vorrichtung zur elektrolytischen
Behandlung von Flüssigkeiten.

Verfahren zur Entfernung von elektro-
lyten aus kolloiden Lösungen
und Gallerien.

Procédé et appareil pour la
purification de fluides.

Epurateur d'eau.

Procédé d'épuration de l'eau et
autres liquides par électrodialyse,
et dispositifs pour la réalisation
de ce procédé.

Verfahren zur Entsalzung von Flüs-
sigkeiten auf elektrischem Wege.

Verfahren und Apparat zur Elektri-
schen Entsalzung von Flüssigkeiten.

A.T.A.-T.N.O.
T.A. No 270.
Appendix 5.

Dutch Pat. 29,194

Appl. 16-2-1933

Prior Germany 12-4-1929

J. Billiter, Vienna.

Dutch Pat. 37,219

= British Pat. 398,751.

Appl. 17-12-1935

Prior Belgium 26-3-1932

Karl.Kaisser, München.

Dutch Pat. 51,142

= British Pat. 507,597

Appl. 16-11-1941

Prior Belgium 19-12-1936

= French Pat. = 830,599

J.W.A. Convert, Brussels.

P.P.J.F. Mommen, Brussels.

Werkwijze en inrichting voor
nigen van zoutarme oplossin-
gen van vloeistoffen op
behulp van de elektrische :

Inrichting voor het electro-
zuiveren van vloeistoffen,
melijk water.

Inrichting voor het electro-
onttrekken of concentreren
een vloeistof opgeloste of
deerde stoffen aan (in) een
sing of een mengsel.

A.T.A.-T.
T.A. No
Appendix

Calculation of the current density of a monovalent ion in a membrane placed between two solutions with different monovalent ions, using Planck's method, as carried out by Teorell (90).

Planck's fundamental equation for a monovalent type of ion (92)

$$i' = - u' \cdot a' \left(\underbrace{\frac{R T}{a'} \cdot \frac{dc}{dx}}_{\text{osmotic term}} \pm \underbrace{\frac{F}{dx}}_{\text{electric term}} \right)$$

After introducing Planck's constant:

$$\zeta = e^{(F/RT)_E}$$

this equation becomes for the cations, present in the solution membrane, e.g.:

$$i^+ = - R \cdot T \cdot u^+ \cdot a^+ \cdot \frac{d \ln(a^+ / \zeta)}{dx}$$

and for the anions e.g.:

$$i^- = - R \cdot T \cdot v^- \cdot a^- \cdot \frac{d \ln(a^- / \zeta)}{dx}$$

By introducing the abbreviations A' and B' (Cf. Planck) the following equations are obtained:

$$i^+ = - u^+ \cdot A' \quad (1) \quad \text{and} \quad i^- = - v^- \cdot B' \quad (2)$$

in which, therefore:

$$A' = R \cdot T \cdot a^+ \cdot \frac{d \ln(a^+ / \zeta)}{dx}$$

and

$$B' = R \cdot T \cdot a^- \cdot \frac{d \ln(a^- / \zeta)}{dx}$$

In the stationary state the current density of an ion is the same across the cross section of the membrane, and therefore all A' and all B' constants.

In order to simplify integration of the above equations in the stationary state with certain concentrations on both sides of the membrane, equations (1) and (2) are written as follows:

A.T.
T.A.
App

- 2 -

$$i^+ = -u^+ \left(\frac{A^+}{A} \right) \left(\frac{A}{A+B} \right) (A+B)$$

and

$$i^- = -v^- \left(\frac{B^-}{B} \right) \left(\frac{B}{A+B} \right) (A+B)$$

in which $A = (A^+ + A^{+u} + \dots)$ and $B = (B^- + B^{+u} + \dots)$.

By dealing separately with the factors for the cations A^+/A , $A/A+B$ and $A+B$ we obtain as a result the general equation given on pg 67 and in Table VIII.

The concentrations in this equation are those in the membrane surface. The theory of fixed charges (88) assumes a Donnan equilibrium at each of the two membrane surfaces, so that:

$$\frac{a^+}{c^+} = \frac{a^{+u}}{c^+} = \dots = \frac{a^+}{c^+} = \frac{c^-}{a^-} = \frac{c^{-u}}{a^-} = \dots = \frac{c^-}{a^-} = r$$

The Donnan ratio r can be calculated from the "membrane concentration", χ , and the total (exterior) concentration a with the aid of the equation:

$$r = \sqrt{1 + \left(\frac{\omega \bar{x}}{2c} \right)^2 - \left(\frac{\omega \bar{x}}{2c} \right)^2}$$

Simple calculation of the current density efficiency.

I. The two-ion-system (M^+ and R^-).

$$i^+ = u \cdot \gamma^+ \cdot \frac{dE}{dx} - D^+ \cdot \frac{d\gamma^+}{dx}$$

and

$$i^- = v \cdot \gamma^- \cdot \frac{dE}{dx} - D^- \cdot \frac{d\gamma^-}{dx}$$

If:

$$D^+ = \frac{R\tau}{F} \cdot u \quad \text{and} \quad D^- = -\frac{R\tau}{F} \cdot v,$$

then:

$$i = i^+ + i^- = (u \gamma^+ + v \gamma^-) \frac{dE}{dx} - \frac{R\tau}{F} (u \cdot \frac{d\gamma^+}{dx} - v \cdot \frac{d\gamma^-}{dx})$$

As the specific conductance χ is equivalent to $u \cdot \gamma^+ + v \cdot \gamma^-$, then

$$i = \chi \cdot \frac{dE}{dx} - \frac{R\tau}{F} \cdot \frac{d}{dx} (u \gamma^+ - v \gamma^-)$$

As $\gamma^+ = -\gamma^-$ therefore

$$\frac{d}{dx} (u \gamma^+ - v \gamma^-) = (u + v) \cdot \frac{d\gamma^+}{dx}$$

and

$$\frac{dE}{dx} = \frac{i}{\chi} + \frac{R\tau}{\chi \cdot F} \cdot (u + v) \cdot \frac{d\gamma^+}{dx}$$

This term for the field strength substituted in the above equations for i^+ and i^- gives:

$$i^+ = \frac{u + I^+}{\chi} \cdot i + \frac{u \cdot \gamma^+}{\chi \cdot F} \cdot R\tau \cdot (u + v) \cdot \frac{dI^+}{dx} - \frac{R\tau}{F} \cdot u \cdot \frac{d\gamma^+}{dx}$$

therefore:

$$i^+ = \frac{u}{u - v} \cdot i + \frac{u}{u - v} \cdot \left\{ (u + v) - u \cdot \frac{R\tau}{F} \cdot \frac{d\gamma^+}{dx} \right\}$$

The transference number of the M^+ -ions, n^+ , is equal to $\frac{u}{u-v}$, therefore:

$$i^+ = n^+ \cdot i + \frac{2uv}{u-v} \cdot \frac{RT}{F} \cdot \frac{d\gamma^+}{dx}$$

$$i^+ = n^+ \cdot i + \frac{2v}{u-v} \cdot D^+ \cdot \frac{d\gamma^+}{dx}$$

$$\text{As } \frac{v}{u-v} = \frac{D^-}{D^+ + D^-}, \text{ then } i^+ = n^+ \cdot i + \frac{2 \cdot D^+ \cdot D^-}{D^+ + D^-} \cdot \frac{d\gamma^+}{dx}$$

If we now introduce the mixed diffusion coefficient of the salt MR:

$$D^* = \frac{2D^+ \cdot D^-}{D^+ + D^-}$$

then:

$$i^+ = n^+ \cdot i + D^* \cdot \frac{d\gamma^+}{dx}$$

Hence follows for the current density efficiency:

$$\eta_M^i = \frac{i^+}{i} = n^+ + \frac{D^*}{i} \cdot \frac{d\gamma^+}{dx}$$

Integration (limits γ_1 and γ_2 , $x_1 = 0$ and $x_2 = \delta$) gives

$$\eta_M^i = n^+ + \frac{D^*}{i \cdot \delta} \cdot (\gamma_2 - \gamma_1)$$

II. The three-ion-system (M^+ , N^+ and R^-).

Although fundamentally the same, deduction is much more complex. Because two independent ion concentrations come into the equations, integration is necessary twice.

We consider first the current densities of the M^- , the N^+ - and the R^- ions, i^+ , i^+ and i^- .

Now: (1) $i^+ = u^+ \cdot \gamma^+ \cdot \frac{dE}{dx} - D^+ \cdot \frac{d\gamma^+}{dx}$, in which

$$(2) D^+ = \frac{RT}{F} \cdot u^+,$$

thus

$$(3a) i^+ = u^+ \cdot \gamma^+ \cdot \frac{dE}{dx} - \frac{RT}{F} \cdot u^+ \cdot \frac{d\gamma^+}{dx}$$

Similarly:

$$(3b) i^+ = u^+ \cdot \gamma^+ \cdot \frac{dE}{dx} - \frac{RT}{F} \cdot u^+ \cdot \frac{d\gamma^+}{dx},$$

and

$$(3c) i^- = v \cdot \gamma^- \cdot \frac{dE}{dx} + \frac{RT}{F} \cdot v \cdot \frac{d\gamma^-}{dx}$$

Totalling i^+ , i^+ and i^- gives the current density in the pores i :

$$i = (u^+ \cdot \gamma^+ + u^+ \cdot \gamma^+ + v \cdot \gamma^-) \cdot \frac{dE}{dx} - \frac{RT}{F} \cdot (u^+ \cdot \frac{d\gamma^+}{dx} + u^+ \cdot \frac{d\gamma^+}{dx} - v \cdot \frac{d\gamma^-}{dx})$$

Now:

$$(4) u^+ \cdot \gamma^+ + u^+ \cdot \gamma^+ + v \cdot \gamma^- = \chi$$

and

$$(5) u^+ \cdot \gamma^+ + u^+ \cdot \gamma^+ - v \cdot \gamma^- = \chi - 2v \cdot \gamma^-$$

thus

$$i = \chi \cdot \frac{dE}{dx} - \frac{RT}{F} \cdot \frac{d(\chi - 2v \cdot \gamma^-)}{dx}$$

From this $\frac{dE}{dx}$ can be solved:

$$(6) \frac{dE}{dx} = \frac{i}{\chi} + \frac{RT}{F\chi} \cdot \frac{d(\chi - 2v \cdot \gamma^-)}{dx}$$

It will be seen from this that the actual field strength $(\frac{dE}{dx})$ is equivalent to the Ohmic field strength $(\frac{i}{\chi})$ increased by the field strength imposed to it by diffusion.

With the aid of this expression the actual field strength which always appears in the equation for current density efficiency, is eliminated. The current density efficiency of the R^- ions (η_R^i) is found by dividing i^- and thus equation (3c) by the current density (i) , hence:

$$(7) \quad \eta_R^i = \frac{v \cdot \gamma^-}{i} \cdot \frac{d\chi}{dx} + \frac{R\tau}{F \cdot i} \cdot v \cdot \frac{d\gamma^-}{dx}$$

Substitution of (6) in (7) gives

$$(8) \quad \eta_R^i = \frac{v \cdot \gamma^-}{i} \left\{ \frac{i + R\tau}{\chi + F\gamma} \cdot \frac{d\chi}{dx} - \frac{2 R\tau v}{F \cdot \chi} \cdot \frac{d\gamma^-}{dx} \right\} + \frac{R\tau}{F \cdot i} \cdot v \cdot \frac{d\gamma^-}{dx}$$

This equation contains three variables, viz. χ , γ^- en x . Now $\frac{d\gamma^-}{dx}$, however, is constant, as will be proved below.

If no accumulation of ions is to occur with time, the expression (1) and likewise the two analogous expressions for the N^- - and F^- -ions must yield zero in differentiation towards x , as the relative part of each kind of ion in current transport must be the same in each place. The following equations therefore apply:

$$(9a) \quad \frac{d}{dx} (\gamma^+ \cdot \frac{dE}{dx}) = \frac{R\tau}{F} \cdot \frac{d^2 \gamma^+}{dx^2}$$

$$(9b) \quad \frac{d}{dx} (\gamma^+ \cdot \frac{dE}{dx}) = \frac{R\tau}{F} \cdot \frac{d^2 \gamma^+}{dx^2}$$

$$(9c) \quad \frac{d}{dx} (\gamma^- \cdot \frac{dE}{dx}) = - \frac{R\tau}{F} \cdot \frac{d^2 \gamma^-}{dx^2}$$

Adding these three equations yields:

$$(10) \quad \frac{d}{dx} \left\{ (\gamma^+ + \gamma^+ + \gamma^-) \cdot \frac{dE}{dx} \right\} = \frac{R\tau}{F} \cdot \frac{d^2 (\gamma^+ + \gamma^+ - \gamma^-)}{dx^2}$$

Now because of electroneutrality:

$$\gamma^+ + \gamma^+ + \gamma^- = 0$$

thus

$$\frac{R\tau}{F} \cdot \frac{d^2 (\gamma^+ + \gamma^+ - \gamma^-)}{dx^2} = 0$$

As $\gamma^+ + \gamma^+ - \gamma^- = -2\gamma^-$ this is identical to $\frac{d^2 \gamma^-}{dx^2} = 0$, from which follows

$$\frac{d\gamma^-}{dx} = \text{constant} = p \quad \text{and} \quad \gamma^- = px + q$$

The constants p and q are determined by the concentrations in compartments 1 and 2 and the thickness of the membrane (δ):

$$\gamma^- = \frac{\gamma_2 - \gamma_1}{\delta} \cdot x + \gamma_1$$

After substitution in equation (8) of $\frac{d\gamma^-}{dx} = p$, and of $dx = \frac{\delta}{p}$, we retain an equation in χ and γ^- . After arrangement these can be written as follows:

$$\chi (R\tau \cdot p \cdot v - \eta_R^i \cdot i \cdot F) + \gamma^- (v \cdot i \cdot F - 2 R\tau \cdot p \cdot v^2 + \gamma^- \frac{d\chi}{dx} \cdot R\tau p \cdot v) = 0 \quad (11)$$

This is a differential equation of the type:

$$(12) \quad \gamma^- \cdot \frac{d\chi}{d\gamma^-} + A \cdot \chi + B \cdot \gamma^- = 0$$

We take $\chi = w \cdot \gamma^-$, then

$$\gamma^- \cdot w + \gamma^-^2 \cdot \frac{dw}{d\gamma^-} + A \cdot w \cdot \gamma^- + B \cdot \gamma^- = 0$$

or

$$\frac{dw}{d\gamma^-} + \frac{(A+1)w + B}{\gamma^-} = 0$$

From this it follows:

$$(13) \quad \frac{d}{d\gamma^-} \left[(A+1)w + B \right] + \frac{(A+1) \cdot (A+1)w + B}{\gamma^-} = 0$$

In the latter equation we multiplied by $(A+1)$ on the understanding that:

$$(13a) \quad (A+1) \neq 0$$

Integration of (13) gives:

$$C \left\{ (A+1)w + B \right\} \gamma^{-}^{(A+1)} = 0 \quad (C = \text{integration constant})$$

or

$$C \left\{ (A+1)w + B \right\} \gamma^{-}^{(A+1)} = 1$$

or

$$(14) \quad C \left\{ (A+1)X + B \cdot \gamma^{-} \right\} \gamma^{-}^A = 1.$$

By writing down equation (14) for compartment 1 and for compartment 2 the integration constant can be eliminated. Unless

$$(14a) \quad (A+1)X + B \cdot \gamma^{-} = 0, \text{ i.e. } C = CO$$

This is, we should note, the very case if we convert the three-ion-system into a two-ion-system (see appendix 7, section III). Only in this event therefore the following elimination is no longer permissible:

$$(15) \quad \frac{\left\{ (A+1)X_2 + B \cdot \gamma_2^{-} \right\} \gamma_2^{-}^A}{\left\{ (A+1)X_1 + B \cdot \gamma_1^{-} \right\} \cdot \gamma_1^{-}^A} = 1$$

In this: $\frac{\eta_R^i \cdot i \cdot \delta}{(\gamma_2^{-} - \gamma_1^{-})D^{-}} + 1$ and $B = -v \left\{ \frac{i \cdot \delta}{(\gamma_2^{-} - \gamma_1^{-})D^{-}} + 2 \right\}$

Substituting this in (15) and introducing the symbol Z having the meaning:

$$Z = \frac{i \cdot \delta}{(\gamma_2^{-} - \gamma_1^{-})D^{-}}$$

we find the following implicit expression for current density efficiency of the R⁺-ion.

$$(16) \quad \frac{X_2(\eta_R^i \cdot Z + 2) - v \cdot \gamma_2^{-} (Z + 2)}{X_1(\eta_R^i \cdot Z + 2) - v \cdot \gamma_1^{-} (Z + 2)} = \left(\frac{\gamma_1^{-}}{\gamma_2^{-}} \right) \quad (\eta_R^i \cdot Z + 1)$$

III. Conversion of three-ion-to two-ion-system.

If $\gamma^{+} = 0$, equation (15) would have to pass over into the equation for the two-ion system. In such case $X = u \cdot \gamma^{+} + v \cdot \gamma^{-} = (v - u) \gamma^{-}$.

Substituting in (15) of $X_2 = (v - u) \gamma_2^{-}$, and $X_1 = (v - u) \gamma_1^{-}$, then

$$(17) \quad \frac{\eta_R^i \cdot i \cdot \delta}{(\gamma_2^{-} - \gamma_1^{-})D^{-}} + 2 = 0, \text{ or } \eta_R^i = -\frac{2D^{-}}{\delta} (\gamma_2^{-} - \gamma_1^{-})$$

Equation (17) however means: $A + 1 = 0$, and this is in conflict with condition (13a).

The solution (17) can therefore be introduced into the conversion (13)-(13a). The correct solution for the two-ion-system is found by substituting the expression $X = (v - u) \gamma^{-}$ in (12). We then obtain:

$$(v - u) \gamma^{-} + A(v - u) \gamma^{-} + B \gamma^{-} = 0,$$

from which γ^{-} as a variable is eliminated. Equation (18)

$$(v - u) + A(v - u) + B = 0$$

gives at once the solution which, after substitution of A and B acquires the following form:

$$(19) \quad \eta_R^i = n_R - \frac{D^{\#}}{i \cdot \delta} (\gamma_2^{-} - \gamma_1^{-})$$

$$\text{In this } D^{\#} = \frac{2 \cdot D^{+} \cdot D^{-}}{D^{+} + D^{-}} \text{ and } n_R = n_R \frac{v}{v - u} \text{ (transference number).}$$

Solution (19) has already been obtained in the direct treatment of the two-ion-system.

This solution is now just identical however to the equation (14a) (Compare equation 14a with equation 18), at least for a two-ion-system. Proper elimination of the integration constant is impossible (see equation (15)) because this constant becomes CO. This is therefore the explanation why equation (16) is no longer applicable to the two-ion-system.

Date: April 3 rd, 1952		Electrodialysis experiment nr 49 x)			
Apparatus B ₂ ^R x)		Supplied	Carried off		Rate(1/h)
Anolyte		29 meq NaCl/l	not measured		5 dos.
Catholyte		30 meq NaCl/l	not measured		5 dos.
Dialysate		2000 g 30 meq NaCl/l	1975 g $\left\{ \begin{array}{l} 9 \text{ meq Cl}^-/\text{l} \\ 0.2 \text{ meq OH}^-/\text{l} \end{array} \right.$	13 ciro.	
Membranes		Anodic: T.N.O.- A 21 ¹		Cathodic: T.N.O.- A 22 ¹	
Time (min.)	Temperature (°C)	Current strength (amp.)	Voltage (v)	Current consumption (amp.hr)	Energy consumption (Whr)
0	14	1.5	4.5		
10	14	1.5	4.6	0.25	1.13
20	14	1.5	4.7	0.25	1.16
30	14	1.5	4.8	0.25	1.19
40	14	1.5	4.9	0.25	1.21
50	14	1.5	5.2	0.25	1.26
55	14	1.5	5.5	0.13	0.67
Total				1.38	6.62
Average			4.8		
Energy consumption by extrapolation: $W_0 = W(28,8) = 3.1$					
Amp.hr consumption		1.38, so $q(30,9) = 180 \text{ g NaCl}/100 \text{ amp.hr}$			
x) Thickness of the compartments: 1 mm					
Membrane area: 500 cm ²					
Current density: 2.6 ma/cm ²					
A.T.A.-T.N.O. T.A.No. 270 Appendix 8.					

Electrodialysis experiment nr 50					
Apparatus: B ₂ ^R	Supplied	Carried off.	Rate (1/h)		
Anolyte	970 g 30 meq NaCl/1	535 g { 86 meq Cl ⁻ /1 (38 meq H ⁺ /1	0.31 dos.		
Catholyte	1890 g 29 meq NaCl/1	1890 g { 27 meq Cl ⁻ /1 (30 meq OH ⁻ /1	1.08 dos.		
Dialysate	2000 g 30 meq NaCl/1	1960 g { 8 meq Cl ⁻ /1 (1 meq H ⁺ /1	10 circ.		
Membranes	anodic: T.N.O.-A 40		cathodic: T.N.O.-A 17 ^b		
Time (min.)	Temperature (°C)	Current strength (amp.)	Voltage (v)	Current consumption (amp.hr.)	Energy consumption (Whr)
0	15	1.5	4.1	-	-
5	15	1.5	4.1	0.125	0.513
10	15	1.5	4.2	0.125	0.518
15	15	1.5	4.3	0.125	0.531
20	15	1.5	4.2	0.125	0.531
25	15	1.5	4.2	0.125	0.526
30	15	1.5	4.2	0.125	0.526
35	15	1.5	4.3	0.125	0.526
40	15	1.5	4.3	0.125	0.538
45	15	1.5	4.3	0.125	0.538
50	15	1.5	4.3	0.125	0.538
55	15	1.5	4.4	0.125	0.543
60	15	1.5	4.4	0.125	0.550
65	15	1.5	4.4	0.125	0.550
70	15	1.5	4.4	0.125	0.550
75	15	1.5	4.5	0.125	0.557
80	15	1.5	4.5	0.125	0.563
85	15	1.5	4.5	0.125	0.563
90	15	1.5	4.6	0.125	0.568
95	15	1.5	4.6	0.125	0.575
100	15	1.5	4.8	0.125	0.581
105	15	1.5	4.8	0.125	0.593
Total Average			4.5	2.625	11.49
Energy consumption 11.49 Whr, so $W(30,8) = 11.49 \times \frac{1}{3} = 3.7 \text{ kWh/m}^3$ by extrapolation: $N_E = W(28,8) = 5.2 \text{ kWh/m}^3$					
Amp.hr consumption 2.625, so $q(30,8) = 99 \text{ g NaCl/100 amp.hr.}$ $\varphi_{an}(30,8) = 50\%$, $\varphi_{cn}(30,8) = 5\%$.					
A.T.A.-T.N.O. T.A.-No 270 Appendix 9.					

Electrodialysis experiment nr 51					
Apparatus: B ₂ ^R	Supplied	Carried off	Rate(1/h)		
Anolyte	30 meq NaCl/l	3 meq H ⁺ /l	7 dos.		
Catholyte	30 meq NaCl/l	4 meq OH ⁻ /l	8 dos.		
Dialysate	2000 g 30 meq NaCl/l	1940 g {10 meq Cl ⁻ /l 0.2 meq OH ⁻ /l}	10 circ.		
Membranes	anodic: T.N.O.- A 40		cathodic: T.N.O.- A 17 ^b		
Time (min.)	Temperature (°C)	Current strength (amp.)	Voltage (v)	Current consumption (amp.hr)	Energy consumption (Whr)
0	18	1.5	4.1	-	-
5	18	1.5	4.3	0.125	0.525
10	18	1.5	4.4	0.125	0.543
15	18	1.5	4.4	0.125	0.550
20	18	1.5	4.4	0.125	0.550
25	18	1.5	4.5	0.125	0.557
30	18	1.5	4.5	0.125	0.563
35	19	1.5	4.6	0.125	0.568
40	19	1.5	4.6	0.125	0.575
45	19	1.5	4.7	0.125	0.581
50	19	1.5	4.8	0.125	0.593
55	19	1.5	5.0	0.125	0.613
Total Average			4.5	1.375	6.22
Energy consumption 6.22 Whr, so W(30,10) = 6.22 x $\frac{1}{10}$ = 3.1 kW/m ³ by extrapolation: N _g = W(28,8) = 3.1 kWh/m ³ Amp.hr consumption 1.375, so q(30,10) = 174 (g NaCl/100 amp.hr)					
A.T.A.-T.N.O. T.A.-No 270 Appendix 10.					